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ACIDIC STRUCTURAL GROUPS IN ILLINOIS COALS:

Variation During Oxidation and Carbonization

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J. M. Harris
G. R. Yohe

REPORT OF INVESTIGATIONS 212

ILLINOIS STATE GEOLOGICAL SURVEY
JOHN C. FRYE, *Chief*
URBANA, ILLINOIS

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ACIDIC STRUCTURAL GROUPS IN ILLINOIS COALS: Variation During Oxidation and Carbonization

T. P. Maher, J. M. Harris, and G. R. Yohe

ABSTRACT

Changes of acidity taking place during carbonization of both fresh and oxidized coals were studied to secure new information on the processes of coal carbonization, coal oxidation, and on the effect of oxidation on coking properties.

Three high-volatile Illinois coals and a low-volatile Eastern coal were ground to minus 40-mesh particle size, and separate portions of these were subjected to air oxidation for 64 days at 25°C ("natural" oxidation) and for 47 days at 110°C ("forced" oxidation). Laboratory-scale carbonization of the fresh and oxidized coals was performed at temperatures ranging from 200°C to 600°C. Variations in the contents of acidic structural groups during oxidation and carbonization of these coals were measured by means of potentiometric titration with sodium aminoethoxide in ethylenediamine, using antimony electrodes. Chemical analyses and infrared spectra were also obtained.

All the coals studied behaved as dibasic acids in ethylenediamine. Natural oxidation caused an initial decrease in acidity, followed by a slow rise. Forced oxidation caused a substantial rise in acidity, especially in the more strongly acid groups. Formation of carboxyl groups was indicated in the high-volatile coals.

In the carbonization of the high-volatile coals the original acidic groups began to decrease at temperatures above 200° C. The greatest decrease was from 400° to 500° C, but very weak groups were detected between 300° and 500°C, and their number and the temperature range over which they were found varied considerably in the fresh and oxidized coal carbonization products. The tendency of weak acidic groups to appear seemed to diminish as the rank of the coal increased. They were not found in the carbonization of the low-volatile coal.

INTRODUCTION

Acidic structural groups in fresh bituminous coals are generally considered to be largely phenolic hydroxyl groups, but in oxidized coals there are also carboxyl groups. Such functional groups have been studied by a number of investigators who used a variety of methods, some of which have been reviewed recently by D. W. van Krevelen and J. Schuyer (1957a). Other methods have been described by G. R. Yohe and Eva O. Blodgett (1947), J. K. Brown and W. F. Wyss (1955), and E. P. Uporova and S. R. Rafikov (1956). It should be noted that alcoholic hydroxyl groups, if present, would also be determined by some of the methods used.

The biggest problem in all the methods is the relative inaccessibility of the structural groups. The determination of some of the groups requires a long reaction time (up to a week), and the very fine grinding leads to difficulties in the experiments (for example, in filtering).

Another difficulty is the fact that the products of topochemical reaction (formed during the determination of functional groups or by the reagent used) may be adsorbed on the surface of the coal substance (E. P. Uporova and S. R. Rafikov, 1956).

In the present investigation, acidic groups were determined by direct titration with sodium aminoethoxide in ethylenediamine. The method has a number of marked advantages. The swelling of bituminous coals in ethylenediamine improves the accessibility of the groups, and a strongly basic medium enhances acidic strength so that very weak acids can be titrated. The method permits differentiation between groups of different acidic strength, and it is convenient and relatively fast.

The analytical method was developed by M. L. Moss, J. H. Elliott, and R. T. Hall (1948) to determine acidic groups of phenolic strength and stronger in pure compounds and in "vinsol" resins. It has since been found applicable to the determination of hindered phenols (M. Katz and R. A.

Glenn, 1952), phenolic esters (R. A. Glenn and J. T. Peake, 1955), an enolic compound (J. D. Brooks and T. P. Maher, 1957), peracids, primary and secondary hydroperoxides and hydrogen peroxide (A. J. Martin, 1957), and certain tetrazole derivatives (T. P. Maher and G. R. Yohe, 1958).

Recently W. E. Walker, J. P. Henry, and H. G. Davis (1958) reported that the technique can be used to titrate certain polyphenols, indole, carbazole, N-phenyl and α-phenyl amides and even 1,2- benzofluorene. Their observation that some quinones give acidic reaction products with ethylenediamine agrees with findings in this laboratory. In titrating a series of coals they found that a small quantity of added carbazole helped to sharpen the final end point, particularly in lignites. They stated that exclusion of oxygen was necessary for titration of the most weakly acid groups.

The method was applied by J. D. Brooks and T. P. Maher (1954, 1957) to estimate acidic groups in a wide range of Australian coals. They also found that during the pyrolysis of a medium rank (83 percent carbon) vitrain, the main loss of acidity occurred between 400° and 500°C. When the same vitrain, freshly ground, was exposed to air at room temperature the oxygen first absorbed appeared to form mainly non-acidic groups. Subsequent exposure of the same sample to air at 105°C caused a steady increase in acidity, but again the initial rapid rise in oxygen content was due mainly to the formation of non-acidic groups.

These results suggested that a systematic study of the changes of acidity in a number of fresh coals during carbonization and in the same coals after "natural" and "forced" oxidation might throw some light on the processes of coal carbonization, coal oxidation, and the effect of oxidation on coking properties.

Acknowledgments

The authors are indebted to Dr. O. W. Rees and the staff of the Section of Analytical Chemistry of the Illinois State Geological Survey for the chemical analyses, to P. E. MacMahon and J. M. Serratosa for the infrared spectra, to J. A. Harrison for the petrographic analyses, to J. A. Simon and others in the Coal Geology Section for help in the collection of samples, and to the managers of the collieries concerned for their cooperation.

PROCEDURES

The methods used for obtaining and treating the coals and preparing the samples for the titrations are as follows.

Collection of Samples

We collected coal Samples M, N, and O at the mines, and Sample P was sent to us by parcel post in answer to a request. Each sample consisted of several blocks of about 10 pounds weight or more of the freshest coal available at the mine concerned. Portions which appeared to have high mineral matter content were rejected. The blocks were placed in cans that were sealed after the air was flushed out with nitrogen. This was done immediately for Samples N and O, within a few hours for M, and on receipt for P (six days after removal from the face).

Sampling

The most suitable block, free from dirt and fractures, was chosen and the outside edges either sawed off with a carborundum saw or chipped off with a hammer to yield a center core of about 5 pounds weight. This was put once through the jawcrusher and left overnight in a large nitrogen-filled desiccator, over calcium chloride, to remove any excess moisture.

The following day the sample was put once through the roll mill, well mixed, and divided into three equal portions.

The first portion was to be the "fresh coal sample." From it a representative sample of about 50 g was taken, sieved through a 40-mesh sieve, the oversize ground to pass, and the whole mixed and bottled under nitrogen for the Gieseler plasticity determination.

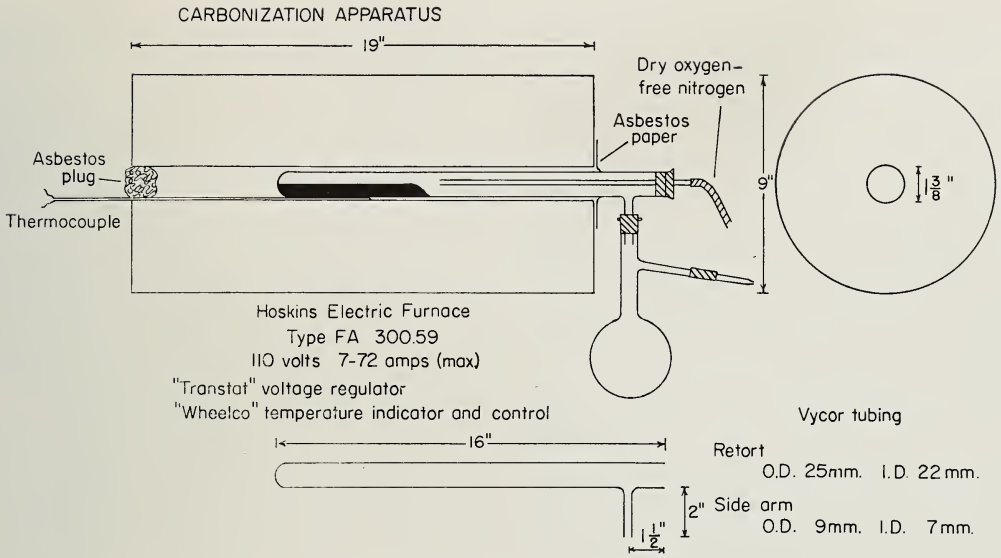


FIG. 1.—Carbonization apparatus.

The remainder of the first portion was reduced to minus 60-mesh by grinding in a nitrogen-filled ball mill and hand grinding of oversize to pass a 60-mesh sieve. The whole was then thoroughly mixed and placed in small bottles, each being filled completely. The bottles held a little more than 50 g so that two carbonization charges could be obtained from each and the small amount left could be discarded.

In preparing the fresh coal sample the cans, jars, bottles, and ball mill that were to contain coal were flushed out with nitrogen before use, and after the sample was put in, if there was a space above it. Exposure to the air was always kept to a minimum.

The second and third portions were prepared for the oxidation experiments by reduction to minus 40-mesh and thorough mixing.

After either natural or forced oxidation, the sampling procedure was the same. The minus 40-mesh oxidized coal was thoroughly mixed and then a representative sample of about 50 g taken from it for the Gieseler plasticity determination. The remainder was reduced to minus 60-mesh, mixed again, and put in small bottles.

OXIDATION

Two methods of controlled aerial oxidation were used:

1) *"Natural" Oxidation.*—Minus 40-mesh coal was spread out in a thin layer on trays and exposed to the air in a room away from light and dust.

The average temperature was about 25°C.

The total time of exposure was 64 days.

2) *"Forced" Oxidation.*—Minus 40-mesh coal was spread out in a thin layer on two trays in a drying oven where it was exposed to air at a temperature of 110°C.

The total time of exposure was 47 days.

In both methods the coal was stirred periodically.

CARBONIZATION

Separate portions of each coal were carbonized to 200°, 300°, 350°, 400°, 450°, 500°, 550° and 600°C.

A Gray-King-type tube furnace was used (fig. 1). A zone at least six inches long could be maintained so that the deviation from the carbonization temperature was never more than ±5°C at any point.

The coal was carbonized in Vycor retorts, the temperature being raised at the rate of 5°C per minute and then held at the selected final temperature for 45 minutes.

Originally, a charge of 20 g of minus 60-mesh coal was used, but later charges were increased to 25 g in order to provide more sample for proximate and ultimate analyses. When a coke swelled outside the zone of uniform temperature, the part outside was discarded. If strong swelling was expected, several carbonizations of 10 g charges were made.

The charges and the chars or cokes formed were weighed to the nearest 0.01 g.

Dry oxygen-free nitrogen was led into the retort to flush it out at the start and the flow was maintained at a very slow rate throughout the carbonization and cooling. The last traces of oxygen in the nitrogen were removed by a bubbler of alkaline anthraquinone β-sodium sulfonate reduced by zinc amalgam. Concentrated sulfuric acid was used to dry the gas.

Fine Grinding

The stainless steel mill described by Yohe and Harman (1941), was used for the very fine grinding required for titration procedure and infrared spectrum determination. Stainless steel rods were used in it instead of balls.

Its construction was such that the air could be flushed out with nitrogen after the sample had been added and the mill closed. About 15 g of minus 60-mesh coal was ground, or the entire product of a carbonization experiment.

Coals and unconsolidated chars were ground overnight; cokes over two nights or even three if they were particularly hard. Cokes were hand ground quickly to a size that the mill could handle. A check by J. A. Harrison on a high-volatile coal showed that overnight grinding from minus 60-mesh reduced 90 percent of it to five microns or less.

The samples after grinding were placed in small bottles, previously flushed out with nitrogen. The nitrogen flushing was also used subsequently, any time that the bottles were opened, to insure removal of oxygen from the gas above the sample.

Titrations

The apparatus and procedures used in the titrations were essentially those described by Brooks and Maher (1957) except for the following modifications:

(1) A Leeds and Northrup student-type potentiometer was used, in conjunction with a Weston Standard cell and a light-scale galvanometer, to measure the E.M.F. This had a range of 0 to 1600 millivolts and a limit reading of one millivolt.

(2) The rate of addition of the titrant was changed to 0.2 ml per 3-minute interval because the former rate of 0.2 ml per 2-minute interval was found to be a little too fast for some samples in which large changes of E.M.F. occurred.

(3) A longer time was allowed for equilibrium to be established before beginning the titration.

Reagents

Monoethanolamine (Carbide and Carbon Chemical Company) was allowed to stand over sodium hydroxide pellets and was purified by triple distillation through a fractionating column packed with ¼-inch porcelain Berl saddles.

Ethylenediamine (Eastman Kodak Company 95-100 percent and Dow Chemical Company 98 percent) was allowed to stand over sodium hydroxide pellets, further purified by refluxing with sodium until the latter was no longer consumed, and then distilled over sodium through a fractionating column packed with Berl saddles using an Ascarite guard tube to exclude carbon dioxide. Azeotropic distillation with benzene was found to be less satisfactory.

Sodium, A. R. (Rascher and Betzold, Inc.) was used as purchased after trimming to remove corroded surfaces.

Antimony metal (Powder) (Baker Chemical Company) was purified by melting it in a crucible, skimming the surface, and pouring off the metal into another crucible. The process was repeated several times.

Sisco 300 Grease (Swedish Iron and Steel Corporation) was used to lubricate all joints

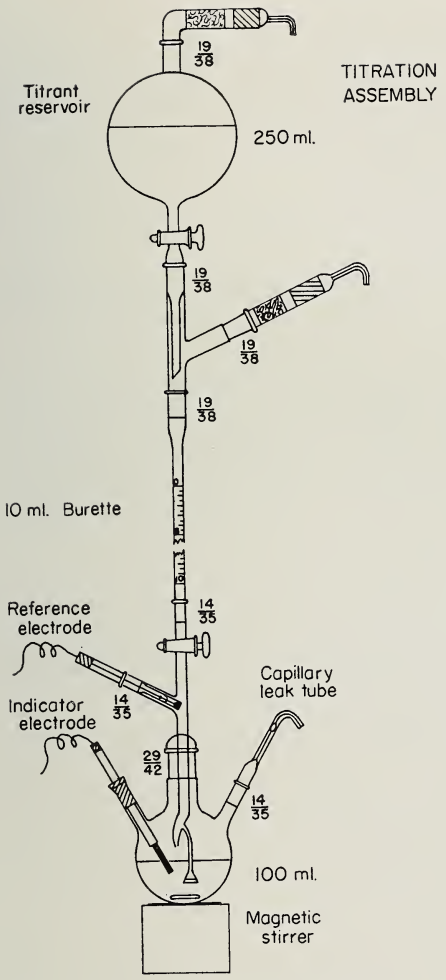


FIG. 2.—Titration assembly. "Fraction" notations designate standard taper joint size.

and stopcocks because of its resistance to ethylenediamine.

Pure benzoic acid (National Bureau of Standards) was used as obtained.

Sodium aminoethoxide titrant (approximately 0.2 N) was prepared in the following manner: Sodium (2.5 grams) was washed successively with small volumes of ethanol and monoethanolamine and dissolved in 100 milliliters of monoethanolamine. The flask was cooled in ice when necessary to slow down the rate of reaction. When all the sodium had dissolved, the solution was made up to 500 ml with anhydrous ethylenediamine. It was standardized against pure benzoic acid.

Apparatus

A diagram of the titration apparatus is shown in figure 2.

The reference electrode was in the titrant stream below the stopcock of the burette. It consisted of a small bead of antimony poured while molten into the cup at the end of the electrode tube and ground off carefully when cool so that the antimony surface was even with the end of the tube. It was connected by a piece of platinum wire, through a glass seal, to the copper lead to the potentiometer. The platinum-copper connection was made with silver solder.

The indicator electrode dipped into the titration flask. It consisted of an antimony rod fitted into a stainless steel rod, the end of which was drilled out to accommodate it. The antimony rod was made by sucking up molten antimony (only a little above the melting point) into a glass tube of appropriate internal diameter by means of a rubber bulb. When the antimony solidified, the glass tube was cracked by holding it in cold water, then it was chipped away from the metal.

The electrical connection between the two electrodes was effected by a narrow glass tube from just above the burette tip dipping below the surface of the liquid in the flask. The bottom end was closed by a fritted glass disc made from an ultrafine microfilter funnel. This was necessary to prevent diffusion of the solution being titrated up to the reference electrode during the slow titrations.

The burette was of 10 ml capacity graduated to 0.05 ml. The limit of reading was 0.01 ml.

Detailed Titration Procedure

The glass-covered stirring bar was placed in the titration flask, the capillary leak tube inserted and the electrode neck plugged with cotton.

Approximately 0.2 g of sample was weighed out accurately and transferred quantitatively through a powder funnel to the flask, the last traces being washed in with 40 ml of anhydrous ethylenediamine. The flask was then stoppered.

The titrant was adjusted to a suitable level in the burette, the protective tube removed from the tip assembly which was then cleaned with several swabs of cotton to remove titrant from the outside, and the flask then put in position.

The end and sides of the antimony rod were polished with a piece of fine grade emery cloth and the adhering antimony powder carefully removed by successive polishings with cotton. The antimony rod was fitted into the stainless steel holder which had previously been fitted through the rubber stopper.

The plug was then removed from the appropriate neck of the flask and the indicator electrode inserted so that about half an inch of the antimony rod was below the surface of the liquid.

The magnetic stirrer was turned on and the indicator electrodes connected to the potentiometer.

Pre-titration Period

The original E.M.F. was measured and the time noted. The value of the E.M.F. depended on the sample being titrated and other factors, but often it was of the order of 550 millivolts. It began to rise steadily. It was measured periodically and the titration was not begun until the system was at equilibrium. This usually required about three hours, and in many cases there was a rise of about 400 mv.

Titration Period

Before starting the titration, the potentiometer was restandardized against the standard cell. The E.M.F. was measured, the time and the burette reading noted. Then approximately 0.2 ml of titrant was added to bring the meniscus to one of the 0.05 ml graduations. The apparatus was lifted slightly, and the flask tapped lightly back on the magnetic stirrer to dislodge any drop hanging on the burette tip. A sheaf of about a dozen filter papers on the top of the magnetic stirrer acted as a cushion and also helped to insulate the flask from any heat developed in the stirrer.

After 2½ minutes, the measurement of the new E.M.F. was begun so that it could be concluded by 3 minutes when another 0.20 ml could be added.

The new E.M.F. was noted, the E.M.F. change recorded, and the E.M.F. change per unit volume of titrant added was calculated.

This procedure was continued until the titration was judged to have been completed.

The stirrer was turned off, the titration flask disconnected and replaced by the protective tube containing titrant after the tip had been cleaned as before. The burette was refilled from the reservoir. This helped keep the inside surface clean. The titration residues were poured into a bottle for later recovery and repurification of the ethylenediamine.

Titration Curve

The titration curve was obtained by plotting the E.M.F. against the volume of titrant added. Inflection points indicated end points in the titration.

The derived graph of change of E.M.F. per unit volume of titrant ($\Delta E/\Delta V$ in the figures) against volume of titrant added, showed the end points as peaks and helped, in conjunction with the titration curve itself, to determine their positions accurately.

From the volume of titrant corresponding to an end point, the acidity could be calculated in milliequivalents per gram of sample.

Determination of Carbon Dioxide in the Ethylenediamine

A blank titration on 40 ml of ethylenediamine was performed weekly to determine the volume of titrant equivalent to its content of carbon dioxide. In this case, the titrant was added in 0.05 ml increments. In the time ordinarily required to use a liter of ethylenediamine the blank usually rose from about 0.05 ml to 0.10 ml. Precautions which helped to keep it low were keeping the neck and stopper of the bottle clean and protected with polyethylene sheeting over cotton, and always withdrawing the solvent by means of a pipette fitted with a rubber bulb.

Standardization of Titrant

The titrant was standardized by titrating about 0.1 g of pure benzoic acid, accurately weighed, in 40 ml of ethylenediamine. In the region of the end point, the titrant was added in 0.05 ml increments. The inflection was very sharp. The value of the blank was subtracted before the normality of the sodium aminoethoxide was calculated. The titrant was standardized periodically.

Infrared Studies

The infrared spectra were determined with a Perkin-Elmer Model 21 double beam spectrophotometer. At first the potassium bromide pellet technique was used for mounting the sample, but it was not found possible to remove completely or to compensate for the water absorbed from the atmosphere while grinding the sample with the potassium bromide. Thus it was uncertain how much of the hydroxyl absorption in the spectrum (at 3600 cm^{-1} to 3100 cm^{-1}) was due to water and how much was actually due to hydroxyl groups in the sample.

A method, based on a suggestion from P. Macdonald (1957), was developed by J. M. Serratosa for obtaining the spectrum in this region by a mixed fluorolube-hexachlorobutadiene mull technique. Fluorolube alone was found too viscous for efficient grinding but hexachlorobutadiene alone tended to evaporate during grinding and was also difficult to use in the cell because of its low viscosity. When the mixed mulling agent was used grinding was efficient, and by the end of the grinding time most of the hexachlorobutadiene had evaporated and the mull had a viscosity which made it suitable for mounting on the sodium chloride window of the cell.

The samples were dried at 110°C in a vacuum pistol over phosphorous pentoxide for about six hours before mulling. The only disadvantage of this technique appeared to be that it was harder to obtain the same sensitivity (judged by the C-H absorption around 3000 cm^{-1}) as in the potassium bromide method. Long grinding times were required.

The assignment of the absorption bands is based in general on work cited by D. W. van Krevelen and J. Schuyer (1957b), R. A. Friedel and J. A. Queiser (1956) and G. Bergmann, G. Huck, J. Karweil, and H. Luther (1957).

RESULTS AND DISCUSSION

"Total Acidity" and "Component Acidities"

Most titration curves had more than one inflection, indicating that groups of different acidic strength were present. The stronger groups titrated first.

The acidity in milliequivalents per gram corresponding to the final inflection has been termed the "total acidity." The amounts of the stronger and weaker groups which add up to give the total acidity have been termed "component acidities" and are always listed in order of decreasing acidic strength (order of titration) across the tables. In the diagrams and figures the order of decreasing acidic strength is arranged from top to bottom.

The reproducibility of component acidities was reasonably good in most tests. An attempt has been made to follow the variation of these component acidities, as well as the total acidity, through each carbonization series. In the tables the component acidity is placed directly below the one at the previous temperature with which it corresponds. In some cases this is easy to see, but in other cases some uncertainty is involved. When a value is put under and between two component acidities of the preceding test, it indicates that differentiation between them is no longer possible.

Acidic Oxygen

Except where otherwise stated, acidic oxygen has been calculated on the basis of one oxygen atom per equivalent of acidity.

SAMPLE M, NO. 6 COAL FROM KNOX COUNTY, ILLINOIS

Sample M was a selected clean specimen of high-volatile C bituminous coal taken from a strip mine operating in the Illinois

No. 6 Coal in Knox County, Illinois. There was about 50 feet of overburden at the site where the sample was taken.

Fresh Coal

The chemical and petrographic analyses, swelling and plastic properties of the fresh coal, and the description and chemical analyses of the chars and cokes obtained from it by carbonization, are given in table 20.

It may be noted that the carbon content of the fresh coal was low (79.60 percent) and the percentage of vitrinite high (95.5 percent). The sulfur content was fairly high (3.21 percent), most (2.17 percent) being in organic form.

Carbonization

Although the swelling properties appeared only moderate (free swelling index 3½), the sample swelled out of the cup during the determination of Gieseler plasticity. The final carbonization product at 600°C was a slightly shrunken hard coke, but the cokes obtained at 400°C and 450°C were highly swollen and frothy. Apparently a slow rate of heating, or holding at temperatures in the plastic range, allowed swelling which was prevented at a faster rate of heating.

The Gieseler maximum fluidity was fairly high (2320 dial divisions per minute), but unreliable because the sample swelled out of the cup.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the fresh coal carbonization series is shown in figure 3.

The total acidity and component acidities at each carbonization temperature are given in table 1, which also gives the total oxygen, acidic oxygen, and the acidic oxygen as percentage of total oxygen.

The fresh coal titration curve had two distinct inflections of large break. The first was due to groups which could not be differentiated from benzoic acid in ethylenediamine in a mixed titration of the coal and the acid. The second was due to groups which were weaker than benzoic acid but stronger than 3,5-dimethylphenol in ethylenediamine.

Up to 350°C the form of the titration curve remained the same, although both component acidities had decreased somewhat.

At 400°C the stronger component acidity was the same as at 350°C, the weaker had further decreased, and a third inflection had appeared in the titration curve, due to groups of still lower acidic strength.

The form of the titration curve was much different at 450°C. The starting E.M.F. was much lower than previously, although a longer time was allowed for equilibration. Three inflections could be distinguished, the first and third being much more definite than the second (which could not be detected on one of the titrations). The first appeared to correspond to what was left of the two strongest component acidities at 400°C. The second apparently corresponded to the new weaker acidity first seen at 400°C, which had increased slightly. The third inflection appeared to be due to very weak groups not formerly present. The small peak at 3.9 ml in the derived graph was thought to be due to an irregularity.

These three inflections could still be distinguished at 500°C, but the relative number of groups responsible for each had changed. Less than half of the first remained, the second had nearly twice as many, and the third remained constant.

At 550°C and 600°C only one inflection was observed. The total break in the curve was much less than for the lower temperature products.

These changes can be seen more clearly by reference to the actual titration curves in figure 3 and are shown diagrammatically in figure 4*a*. In the latter the acidities are given in milliequivalents obtained by multiplying the total and component acidities by the dry ash-free weight of char or coke in each case. This is intended to eliminate changes in acidity per gram that arise only from weight loss during the carbonization. Stronger component acidities are placed above weaker in the histogram.

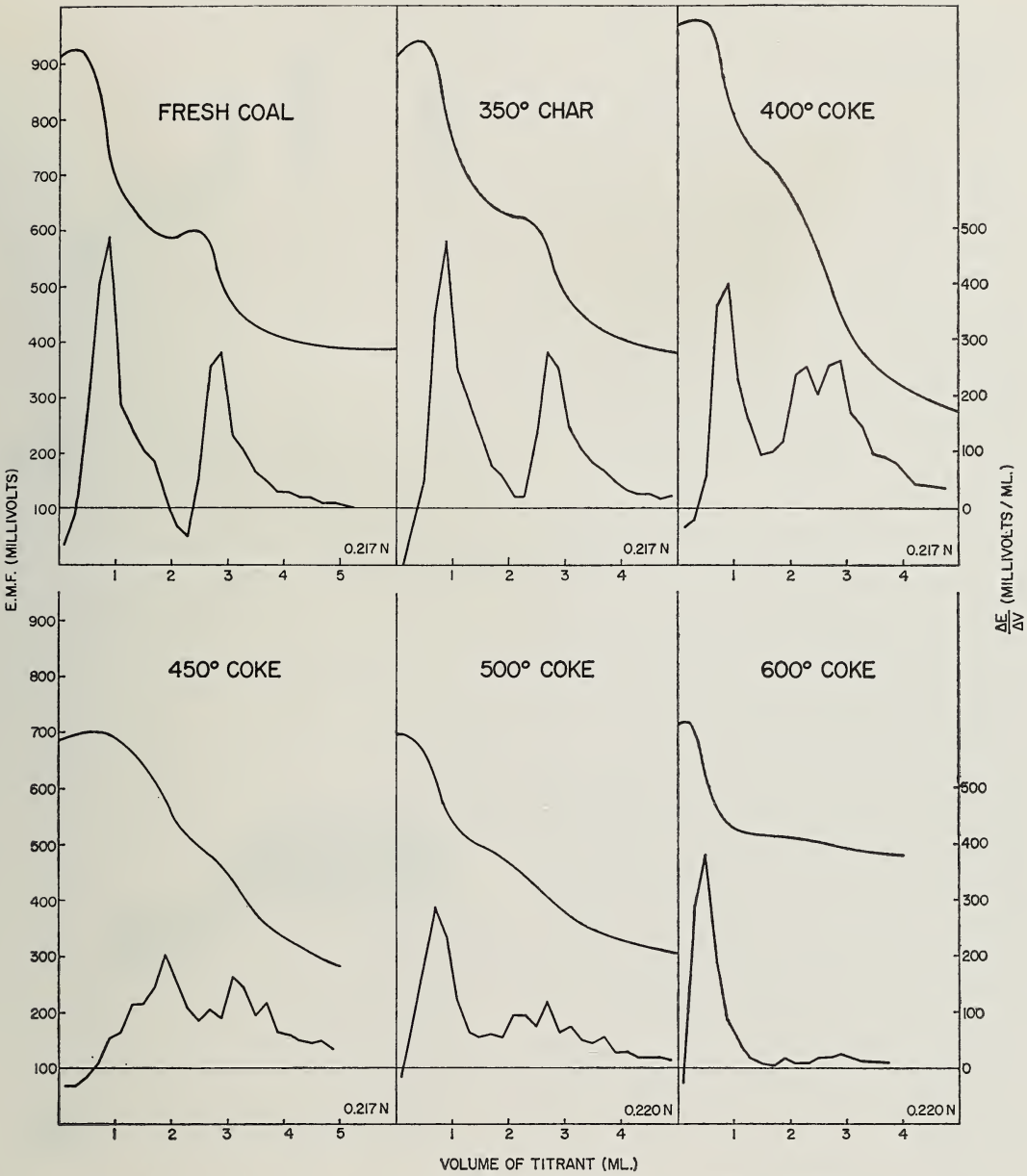


FIG. 3.—Sample M, fresh coal carbonization series: Titration curves and derived graphs.

Figure 4*b* shows the variation in weight of total oxygen and acidic oxygen throughout the carbonization series. It shows that, although the weight of total oxygen fell at a fast, fairly steady rate between 300° and 500°C and then slowed somewhat, the total acidic oxygen fell in two steps. The first was between 250° and 400°C, being fastest a little above 300°C, and the second was between 450° and 550°C, most being lost between 500° and 550°C. The acidic oxygen apparently was converted largely into a non-acidic form, as the weight of non-acidic oxygen increased markedly.

The percentage of oxygen in acidic form was at its maximum at 450° to 500°C where it accounted for almost 80 percent.

Naturally Oxidized Coal

Variation of Acidic Groups During Oxidation

Several determinations of acidic group content were made during the oxidation. The samples were obtained by taking a large number of small increments from different places on the exposed coal and grinding by hand.

The results are shown in table 2. The first determination, made after 18 days, showed that both component acidities had decreased to give a loss of 0.34 milliequivalents per gram in the total acidity. The changes in the rest of the period (up to 64 days) did not appear to be significant.

Carbonization

The analytical data for the carbonization series of the naturally oxidized Sample M are given in table 21.

The only significant difference in the chemical analysis of the oxidized coal from that of the fresh coal was a small decrease in the carbon which slightly increased the oxygen (obtained by difference).

It was noted that during carbonization the oxidized coal lost less of its oxygen but more of its hydrogen at lower temperatures than did the fresh coal. The oxidized coal had slightly lower volatile matter and calorific value but the maximum Gieseler fluidity dropped remarkably (from 2320 to 9 dial divisions per minute) and the plastic range was shorter. The free swelling index however increased (from 3½ to 4).

Carbonization yielded a soft unswollen coke at 400°C, and increase in temperature increased the hardness and caused a slight shrinkage.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the naturally oxidized coal carbonization series is shown in figure 5.

The total acidity and component acidities at each carbonization temperature are given in table 3, which also gives the total oxygen, acidic oxygen, and the acidic oxygen as percentage of total oxygen.

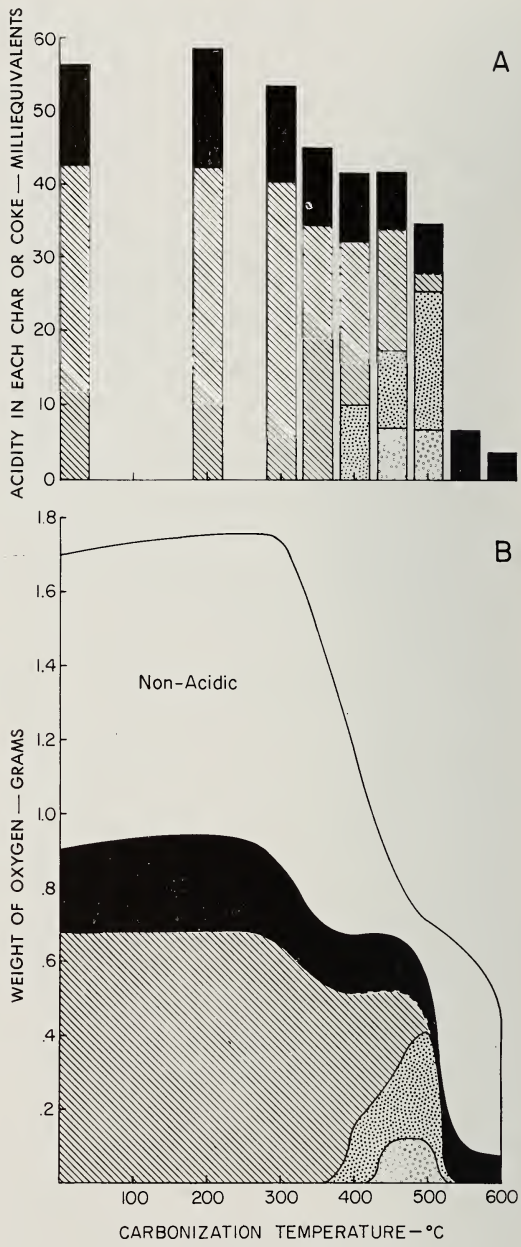


Fig. 4.—Sample M, fresh coal carbonization series:

A. Milliequivalents of total and component acidities in each char or coke.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

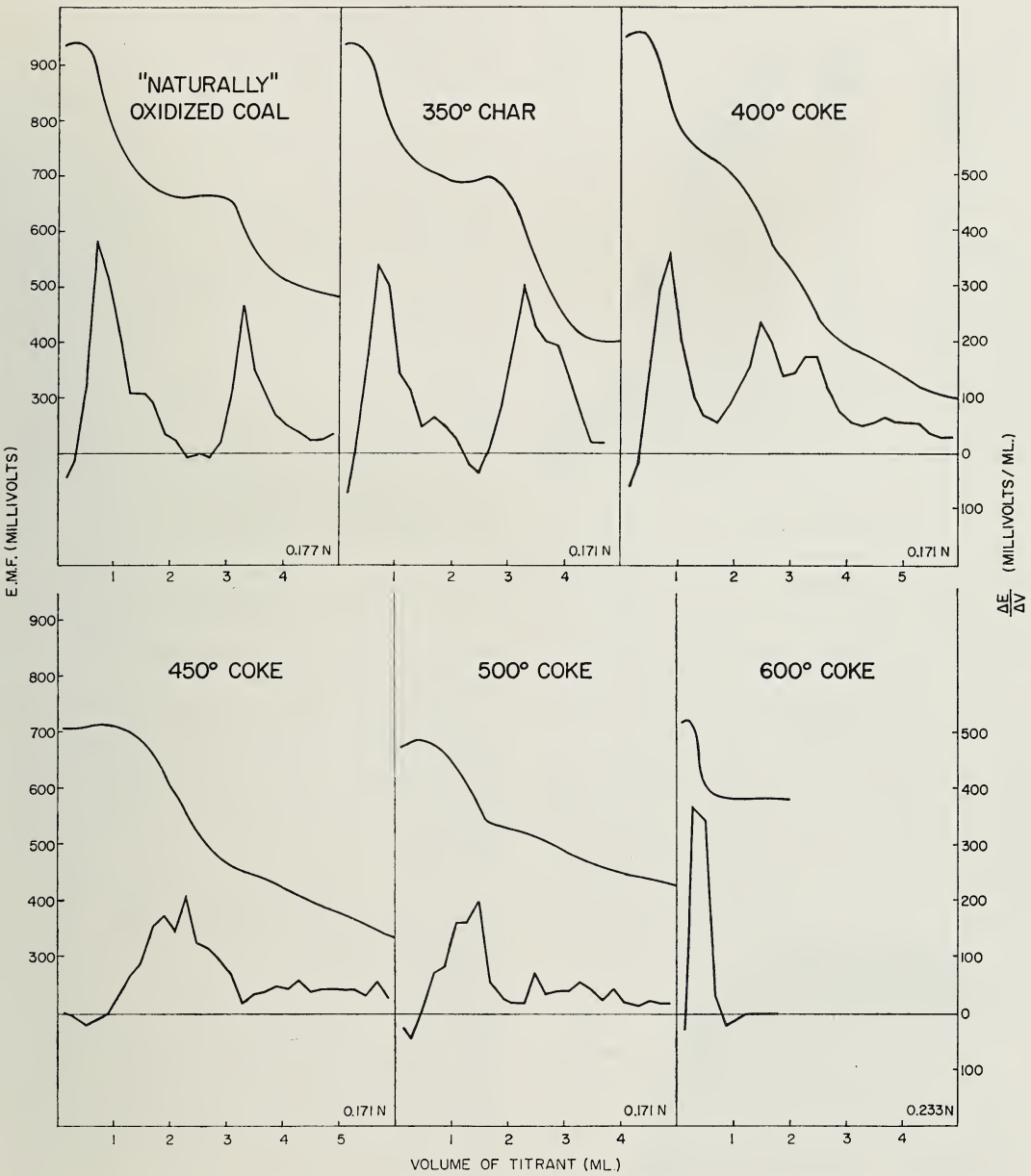


FIG. 5.—Sample M, naturally oxidized coal carbonization series: Titration curves and derived graphs.

The coal itself gave a smooth curve with two sharp inflections. It was similar to that for the fresh coal except that the second inflection occurred at a higher E.M.F.

Up to 350°C the form of the curve was unchanged, but at that temperature each component acidity had decreased slightly. There was also a shoulder on the second peak of the derived graph, seeming to indicate that a small number of still weaker groups were present that could not be differentiated with certainty.

At 400°C this supposition was confirmed by the clear differentiation of a weaker component acidity giving rise to a third inflection in the curve.

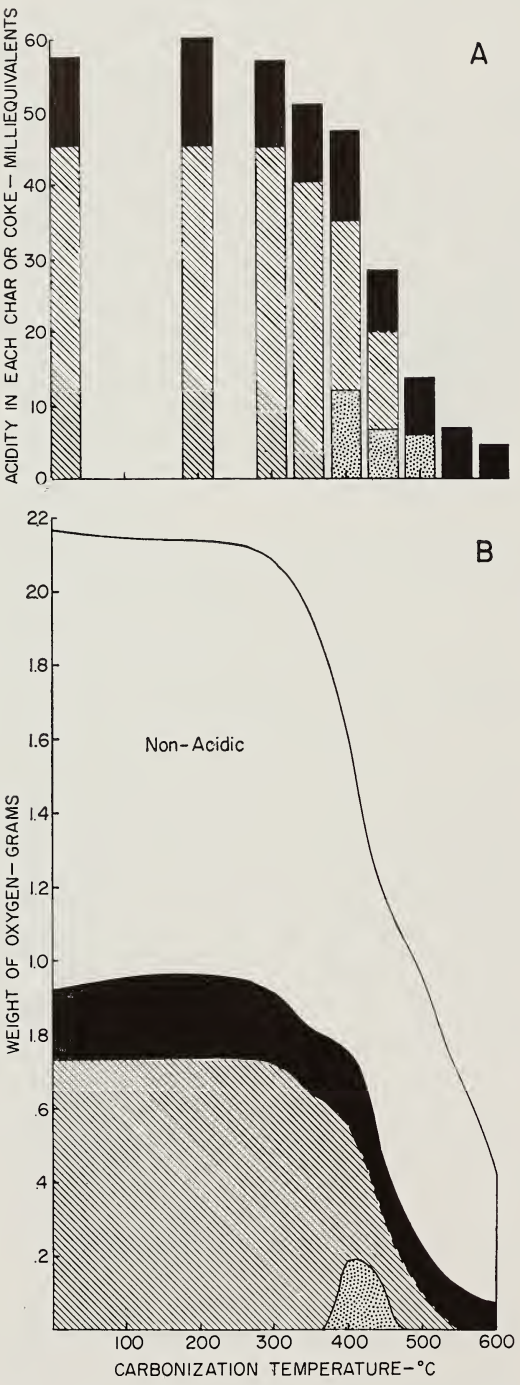


Fig. 6.—Sample M, naturally oxidized coal carbonization series:

A. Milliequivalents of total and component acidities in each char or coke.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

At 450°C, as in the case of the fresh coal, differentiation between the two stronger component acidities was no longer obtained. The other component acidity from 400°C still remained but had decreased in value. The curve in the latter stages was irregular, but showed no further reproducible inflections. Only one inflection was observed at 500°, 550° and 600°C, the acidity gradually decreasing in amount.

Figure 6*a* shows diagrammatically the number of milliequivalents of the component acidities in each char or coke.

The variation in the weight of total oxygen and acidic oxygen throughout the carbonization series is shown in figure 6*b*. It shows that the total oxygen content decreased rapidly between 300° and 450°C and slightly less rapidly between 450° and 600°C. The acidic oxygen disappeared slowly between 200° and 400°C and very rapidly between 400° and 500°C. Little if any of this acidic oxygen appeared to be converted to non-acidic oxygen.

The percentage of oxygen in acidic form in the solid carbonization products was never above 50 percent, reaching its maximum of about 47 percent at 400°C. This was only slightly higher than in the coal itself.

Forced Oxidized Coal

Variation of Acidic Groups During Oxidation

Table 4 shows that there was a gradual increase in the total acidity (from 3.36 to 4.15 milliequivalents per gram) over the 47-day period. The small size of the increase (0.14 milliequivalents per gram) in the first 9 days may have been due to an initial decrease corresponding to natural oxidation.

The stronger component acidity showed a marked increase until finally it could be differentiated into two separate component acidities of slightly different acidic strength.

The weaker component acidity decreased in the first period, then increased by a small amount before decreasing again.

Carbonization

The analytical data for the carbonization series of forced oxidized Sample M are given in table 22.

The oxygen content of the oxidized coal was about twice that of the fresh coal. Throughout the carbonization series the oxygen content was always significantly greater than that of the fresh coal product at the same temperature.

The oxidized coal showed marked decreases in volatile matter (from 49.4 to 39.1 percent) and calorific value (from 14,380 to 11,930 Btu per pound or 7989 to 6628 calories per gram). It was non-swelling and the Gieseler plasticity was unobtainable.

Carbonization yielded no cokes, but gave slightly coherent chars at the higher temperatures.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the forced oxidized coal carbonization series is shown in figure 7.

Of interest is the small but reproducible inflection in the early part of the curve before the first large inflection. It was obtained in the titration of the coal and the 200° and 300° chars. Because of its order of magnitude it is thought to correspond to the stronger component acidity of the fresh coal. The other acidity before the first large inflection would then be due to groups of slightly lower acidic strength formed in the forced oxidation. These are postulated to be carboxyl groups. The presence of such groups is indicated by absorption in the infrared spectrum at 1675-1700 cm^{-1} (carbonyl) for the oxidized coal and for the chars up to 400°C and by the development of pronounced alkali solubility, and it is consistent with the findings of other workers on such oxidized coals.

Differentiation between the two strong component acidities was not achieved at 350° or 400°C although the first inflection now represented an acidity only a little less than the sum of the two formerly present and there was still absorption at 1675-1700 cm^{-1} in the infrared.

The total acidity and component acidities at each carbonization temperature are given in table 5, which also gives the total and acidic oxygen. The acidic oxygen was calculated on the assumption of one atom of oxygen per equivalent of acidity, except for the second strongest component acidity, which was assumed to be due to carboxyl groups as stated above. For this part the acidic oxygen was calculated on the basis of two oxygen atoms per equivalent of acidity. For the 350° and 400°C chars, where differentiation could no longer be seen between the two strong component acidities, approximate values for the acidic oxygen were calculated assuming that the ratio between the groups responsible stayed the same as at 300°C.

The small inflection at about 5.4 ml in the titration curve of the oxidized coal did not appear to be reproducible and was therefore taken to be an irregularity.

The 200° C char gave a titration curve of the same form as the coal but with a slightly lower total acidity.

At 300°C a new inflection due to very weak groups appeared. It was not very sharp, but was reproducible. It persisted up to 450°C, and the acidity corresponding to it increased to 400°C and then decreased.

The initial E.M.F. at 450°C was more than 200 millivolts lower than at 400°C.

At 500°, 550°, and 600°C only one inflection of relatively small break was obtained.

The percentage of oxygen in acidic form reached a maximum at 400°C where it amounted to approximately 75 percent.

Figure 8*a* shows diagrammatically the number of milliequivalents of the component acidities in each char. At 350° and 400°C the strongest component acidity is further divided by a broken line showing the postulated ratio of the two types of groups when they are no longer differentiated in titration.

The variation in the weight of total oxygen and acidic oxygen (based on the assumptions stated earlier) through the carbonization series is shown in figure 8*b*. The region where the amount of carboxyl is uncertain is shown by broken lines.

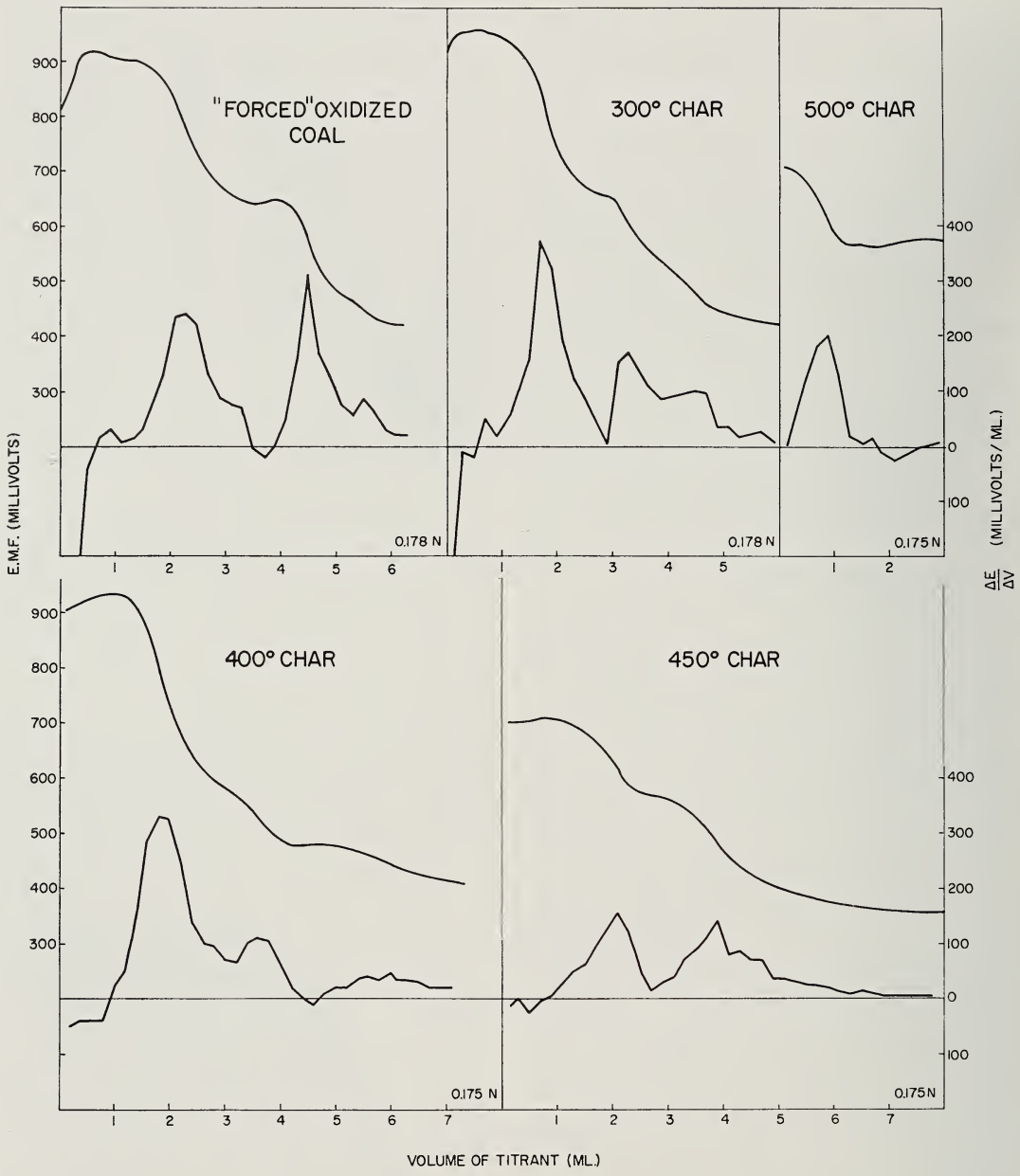


FIG. 7.—Sample M, forced oxidized coal carbonization series: Titration curves and derived graphs.

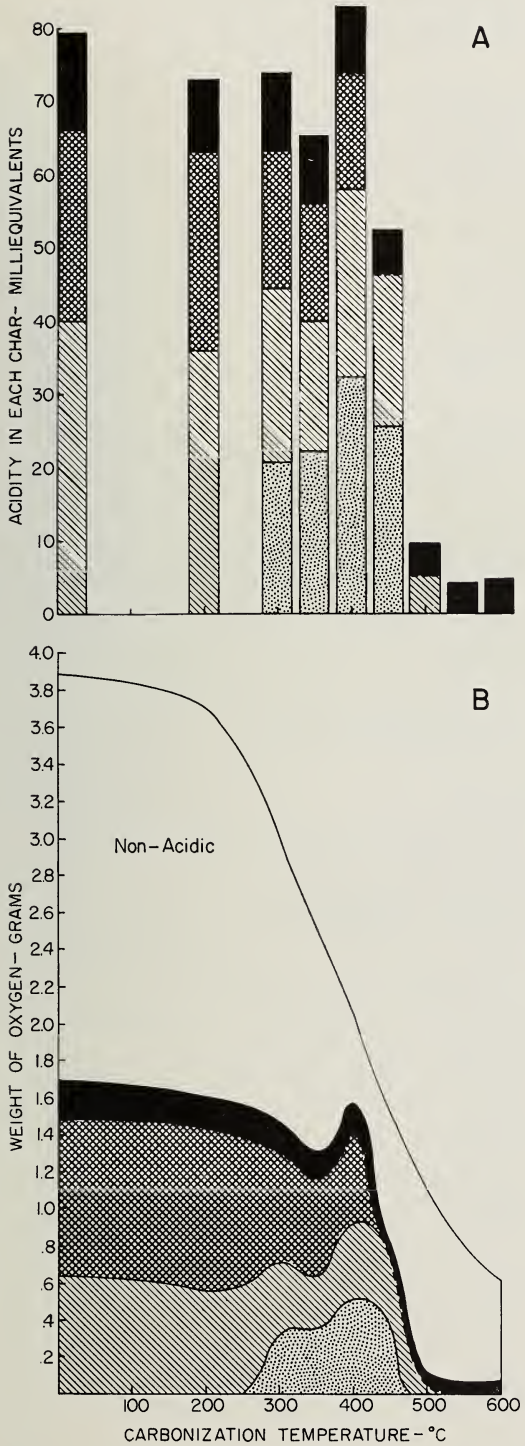


FIG. 8.—Sample M, forced oxidized coal carbonization series:

A. Milliequivalents of total and component acidities in each char.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

Between 350° and 400°C acidic oxygen increased at the expense of non-acidic oxygen but between 400° and 500°C the reverse was the case.

INFRARED SPECTRA

The infrared spectra of fresh, naturally oxidized, and forced oxidized Sample M and of some of the chars and cokes obtained from them are shown in figure 9. All spectra are uncorrected.

Fresh Coal Series

The O-H (and N-H?) absorption band with a very flat "peak" at 3350 cm^{-1} was spread over a large frequency range indicating extensive hydrogen bonding. Judging by the fluorolube spectra, it was fairly strong up to 350°C after which it decreased markedly. However, it still appeared to be present up to 500°C.

There was no indication of aromatic C-H absorption just above 3000 cm^{-1}.

Aliphatic and/or naphthenic (saturated cyclic) C-H stretching absorption of medium strength was found at 2930 cm^{-1} with a shoulder at 2870 cm^{-1}. It decreased slowly to 350°C, rapidly to 400°C, and appeared to be gone at 450° C.

No C:O absorption was found in the 1700 cm^{-1} region.

The characteristic coal absorption band, strong and broad, appeared at 1600 cm^{-1}. It is usually attributed to aromatic structures, perhaps reinforced by conjugated carbonyl groups. It remained throughout the series and although it did decrease, this may have been due to the difficulty of getting a good spectrum with the higher temperature cokes because of the increased scatter.

A band of medium strength with a peak at about 1440 cm^{-1} indicated the presence of aliphatic and/or naphthenic CH_2 and

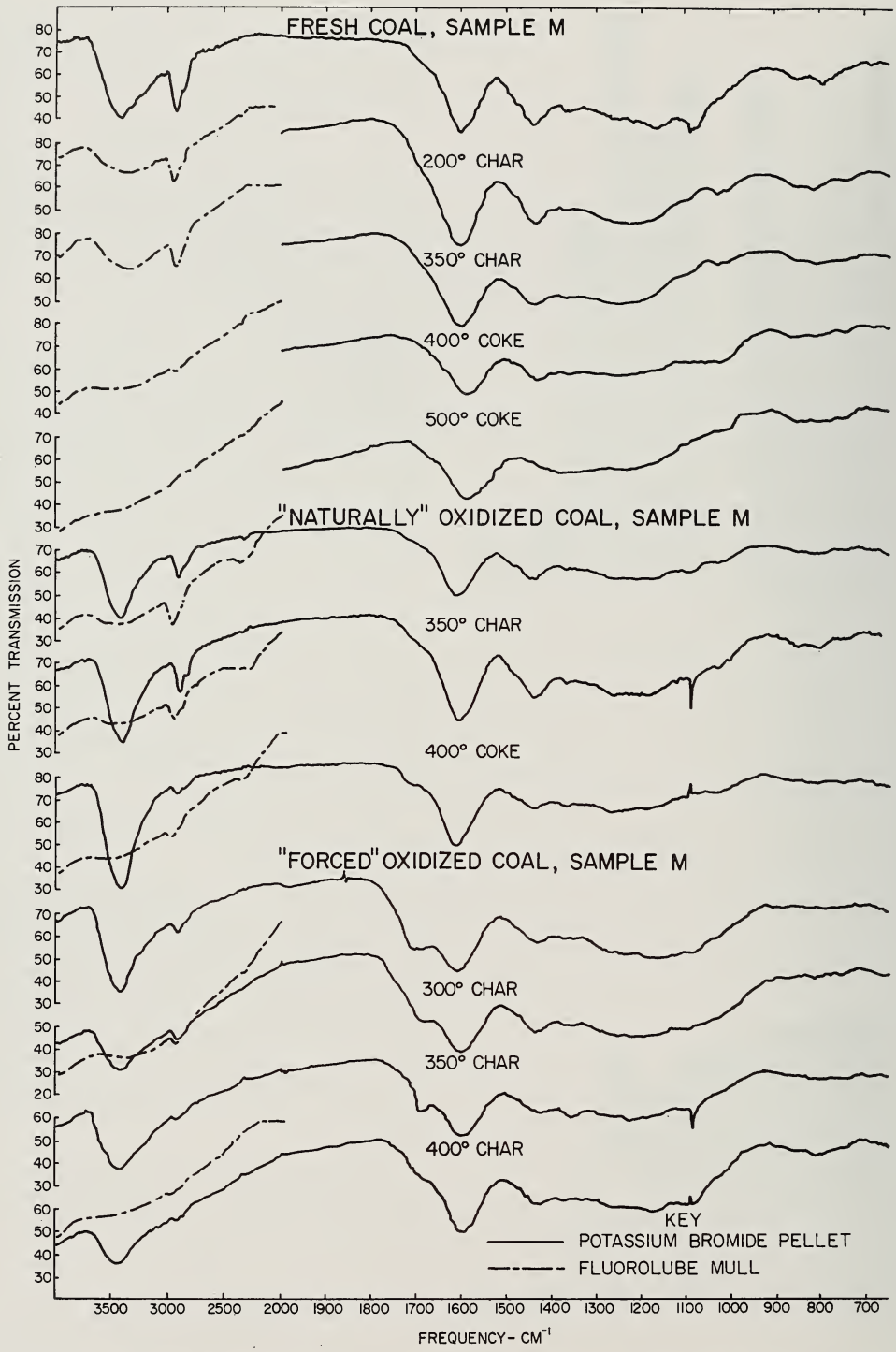


Fig. 9.—Sample M, infrared spectra of the fresh and oxidized coals and some chars and cokes from them.

CH_3 groups. The band began to decrease appreciably after 300°C and appeared to be practically gone at 450°C.

CH_3 groups or cyclic CH_2 groups were also indicated by weak absorption at about 1370 cm^{-1} which became weaker still as the temperature increased, finally disappearing between 400° and 450° C.

No definite assignment could be made for any other absorption bands.

Naturally Oxidized Coal Series

The spectrum of the naturally oxidized coal was not very different from that of the fresh coal.

There was no C:O absorption at about 1700 cm^{-1}, indicating that no significant number of carboxyl groups was formed in the oxidation.

Hydroxyl absorption appeared less strong and the flat peak was at a slightly higher frequency (3440 cm^{-1}). It began to decrease noticeably above 350°C and seemed to have disappeared at 500°C.

The behavior of the other bands throughout the series was substantially the same as for the fresh coal.

Forced Oxidized Coal Series

The most noticeable feature of the spectrum of the forced oxidized coal was the broad shoulder at about 1700 cm^{-1} on the side of the large 1600 cm^{-1} band. It indicated C:O absorption presumably from carboxyl groups formed in the oxidation. At 300° and 350°C in the series it showed as a peak rather than a shoulder, had almost disappeared at 400°C, and could not be seen at 450°C.

It is noteworthy that the absorption due to C-H at 2910 cm^{-1} and CH_2 and CH_3 at 1430 cm^{-1} was much less than in the fresh and naturally oxidized coals. The very weak peak at 1370 cm^{-1} due to the CH_3 or cyclic CH_2 groups was hardly perceptible. This seems to indicate that at least some of the carboxyl groups were formed by the oxidation of these aliphatic or naphthenic groups (cf. B. K. Mazumdar, K. S. Anand, S. N. Roy and A. Lahiri, 1957).

The gradual disappearance of the various other absorption bands with increase of carbonization temperature followed much the same pattern as for the fresh coal.

SAMPLE N, NO. 6 COAL FROM JEFFERSON COUNTY, ILLINOIS

Sample N was a selected clean specimen of high-volatile B bituminous coal taken from an underground mine operating at a depth of about 750 feet in the No. 6 seam in Jefferson County, Illinois.

Fresh Coal

The analytical data for the carbonization series of fresh Sample N are given in table 23.

Although the carbon content (81.59 percent) was two percent higher than for Sample M, the oxygen was also slightly higher. The ash (9.7 percent) and sulfur (0.96 percent) were moderate. More than half the sulfur was organic. The percentage of vitrinite was fairly high (91.6 percent).

Carbonization

The free swelling index (4) was slightly higher than for Sample M, but the Gieseler maximum fluidity was much lower (27 dial divisions per minute) and the plastic range shorter.

Upon carbonization, slightly shrunken cokes were obtained at 450°C and higher. As the temperature was raised, the cokes increased in hardness from moderately hard to hard.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the fresh coal carbonization series of Sample N is shown in figure 10.

The total acidity and component acidities at each carbonization temperature are given in table 6, which also gives the total oxygen and acidic oxygen.

The coal itself gave a smooth curve with two sharp inflections. There was a small rise in E.M.F. after the first inflection, before the fall began for the second. The total acidity was significantly higher than for

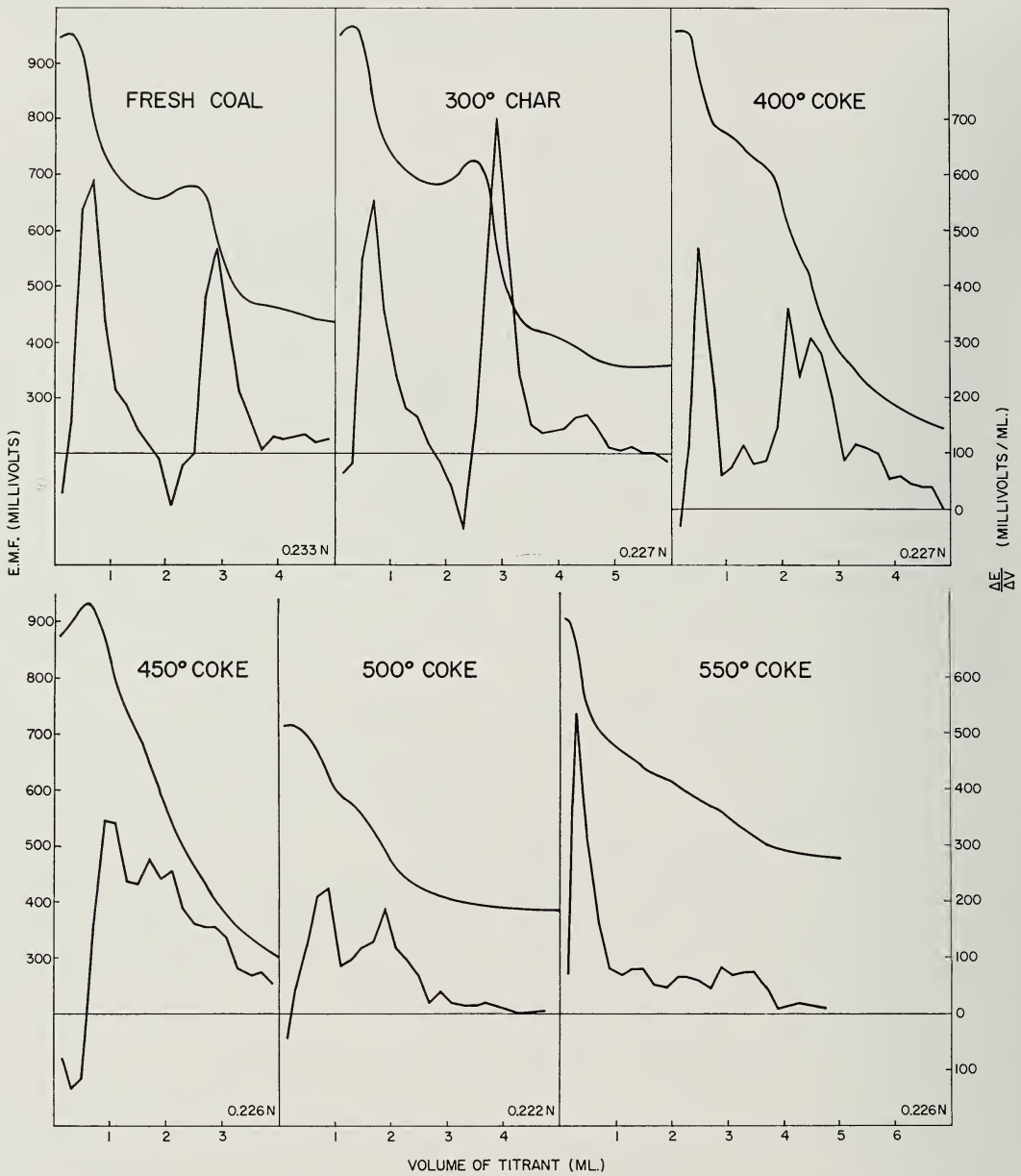


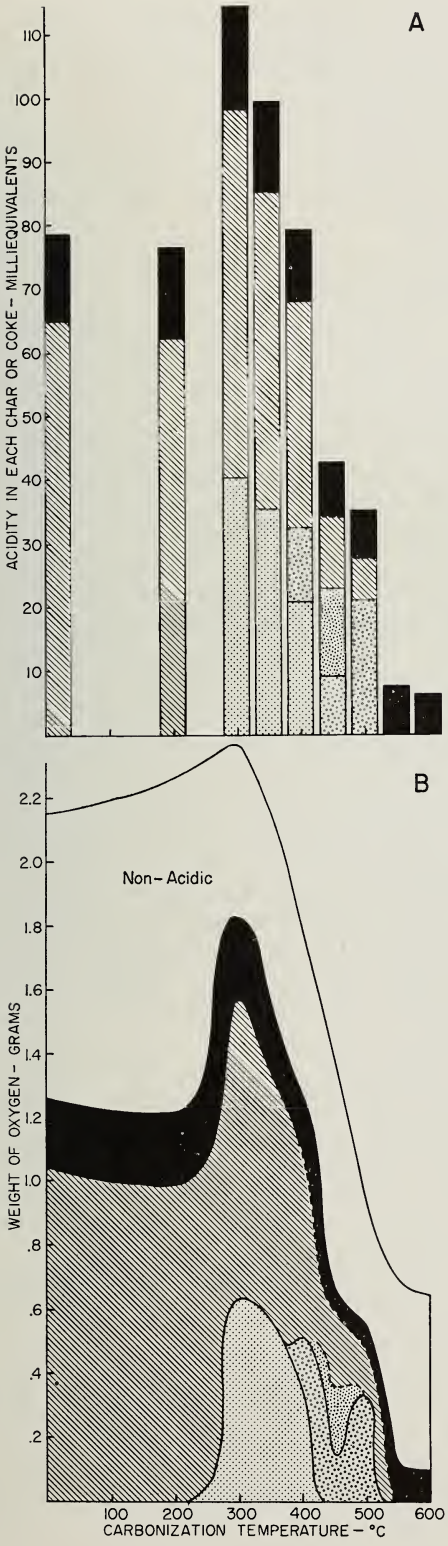
Fig. 10.—Sample N, fresh coal carbonization series: Titration curves and derived graphs.

Sample M which perhaps indicated that acidity correlates with oxygen content rather than carbon content. The stronger component acidity accounted for less of the total than for Sample M.

The form of the curve was the same at 200°C, the weaker component acidity having decreased slightly.

At 300°C a third inflection occurred late in the titration curve. It was not sharp but was reproducible. Apparently it was due to extremely weak acidic groups.

The titration curve at 350°C was of the same form as that at 300°C and had three inflections, the third being very faint. All



component acidities had decreased from their values at 300°C.

At 400°C a fourth inflection appeared, caused by groups stronger than those causing the third inflection, but weaker than those causing the second inflection at 300°C and 350°C. The three component acidities found at these temperatures were still present although their values had decreased still further and the final faint inflection was barely detectable. The small peak at 1.3 ml in the derived graph was due to an interruption in the titration and is not significant.

Three inflections were obtained in the titration curve at 450°C. In the curve shown the starting E.M.F. was over 900 millivolts, the first inflection was very prominent and the other two were very faint. In the other two titrations performed the starting E.M.F. was less than 800 millivolts, the first inflection was not so sharp, and the third inflection was the most prominent. The reason for this variation in behavior is not known, but the reproducibility of the positions of the inflections was reasonably good. The stronger two component acidities appeared to come from the two strongest at 400°C. The weakest component acidity appeared to come from the third strongest at 400°C.

At 500°C only two inflections were obtained. The component acidities appeared to correspond to the strongest and to the sum of the weakest two at 450°C.

At 550°C and 600°C only one inflection was found after which the curve was rather irregular.

Figure 11*a* shows diagrammatically the number of milliequivalents of the component acidities in each char or coke.

The variation in the weight of total oxygen and acidic oxygen throughout the

FIG. 11.—Sample N, fresh coal carbonization series:

A. Milliequivalents of total and component acidities in each char or coke.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

carbonization series is shown in figure 11*b*. The apparent increase in the weight of total oxygen up to 300°C is most probably caused by error due to the use of oxygen values obtained by difference. From 300°C to 550°C the total oxygen dropped rapidly and at a fairly constant rate. This rate decreased markedly between 550°C and 600°C.

The weight of acidic oxygen decreased slightly to 200°C and then increased to about one and a half times this value due to the appearance of the very weakly acidic groups at the expense of non-acidic oxygen. From 300°C to 400°C the acidic oxygen decreased at about the same rate as the total oxygen. The rate was faster to 450°C and then slower to 500°C. In the 500° to 550°C interval the acidic oxygen fell off to a very low value which was only slightly less at 600°C. Non-acidic oxygen increased at the expense of acidic in this range.

The percentage of oxygen in acidic form was greatest at 300°C (over 77 percent) due to the very weakly acidic groups present at that temperature.

Naturally Oxidized Coal

Variation of Acidic Groups During Oxidation

As shown in table 7 there was a fall in total acidity (0.56 milliequivalents per gram) early in the oxidation of Sample N, followed by a rise back almost to the original value.

This occurred with both component acidities also, except that the stronger increased faster than the weaker, and at the end of 44 days was significantly greater than its original value. In the last 20 days it decreased slightly.

Carbonization

The analytical data for naturally oxidized Sample N are given in table 24.

The oxidized coal had a slightly higher oxygen content than the fresh coal but the chars and cokes from it had lower oxygen than the products at the same temperatures from the fresh coal.

The oxidized coal had a slightly lower volatile matter content and calorific value than the fresh coal, the free swelling index was unchanged, but the already low Gieseler plasticity had decreased to a barely measurable amount.

The chars and cokes obtained on carbonization were very similar to those from the fresh coal, perhaps being not quite as hard.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the naturally oxidized coal carbonization series for Sample N is shown in figure 12.

The total acidity and component acidities at each carbonization temperature are given in table 8 which also gives the total oxygen and acidic oxygen.

The oxidized coal gave a smooth titration curve with two sharp inflections which however were not as steep as for the fresh coal. The total acidity had decreased slightly although the stronger component acidity had increased by a small amount.

Up to 300°C the form of the curve remained the same. There was a small decrease in the weaker component acidity.

This component acidity had further decreased at 350°C and a third inflection due to weaker groups made its appearance.

At 400° this new component acidity had increased but of the original two the stronger had decreased slightly and the weaker had only about half its original value.

The initial E.M.F. at 450°C was still above 900 millivolts, but the total break was only about 400 millivolts. There were two inflections, then some irregularities. The first inflection was taken as corresponding to the remnants of the stronger two component acidities at 400°C.

At 500°C and higher temperatures only one inflection was found in the titration curve.

Figure 13*a* shows diagrammatically the number of milliequivalents of the component acidities in each char or coke.

The variation in the weight of total oxygen and acidic oxygen throughout the carbonization series is shown in figure 13*b*.

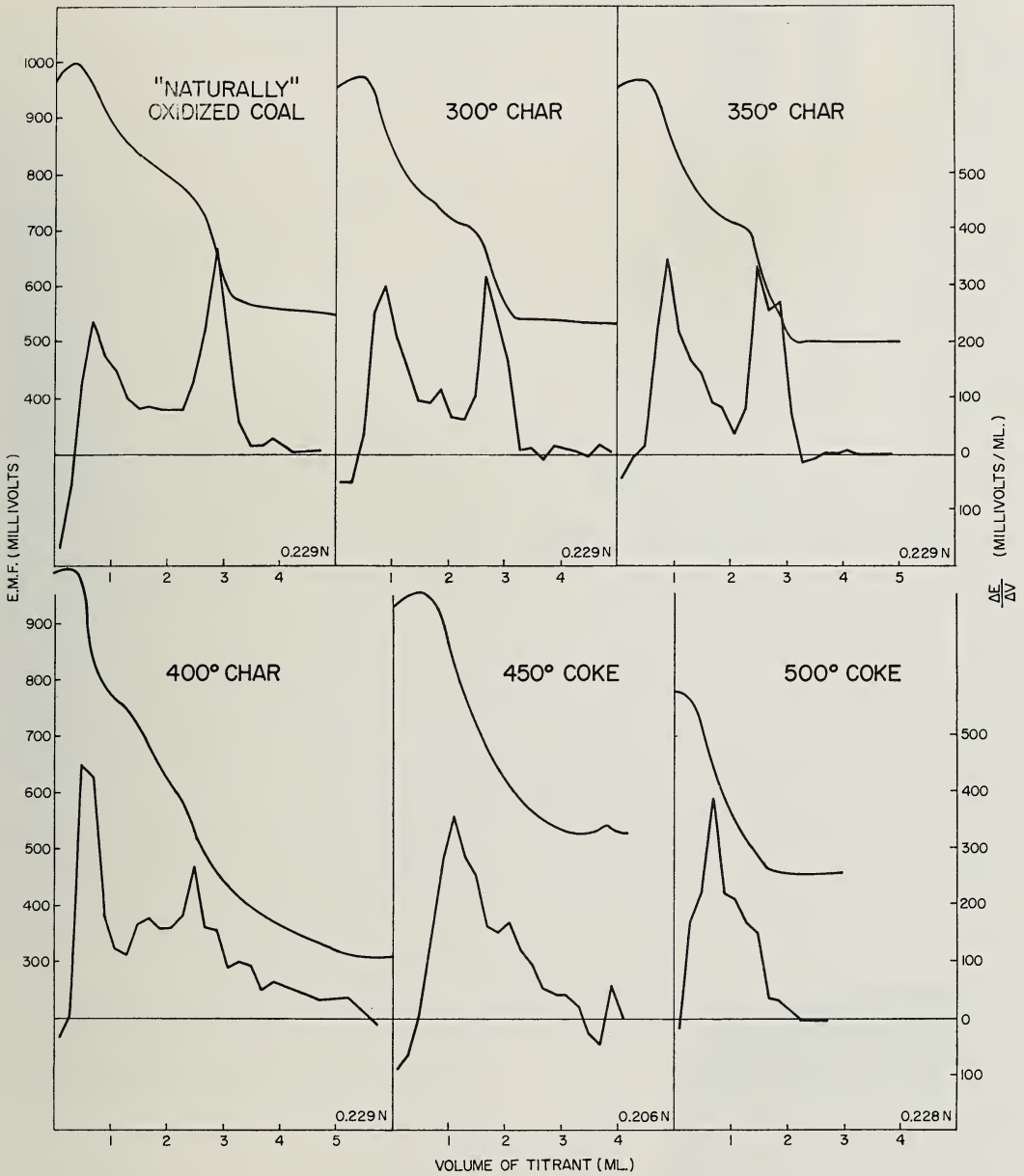
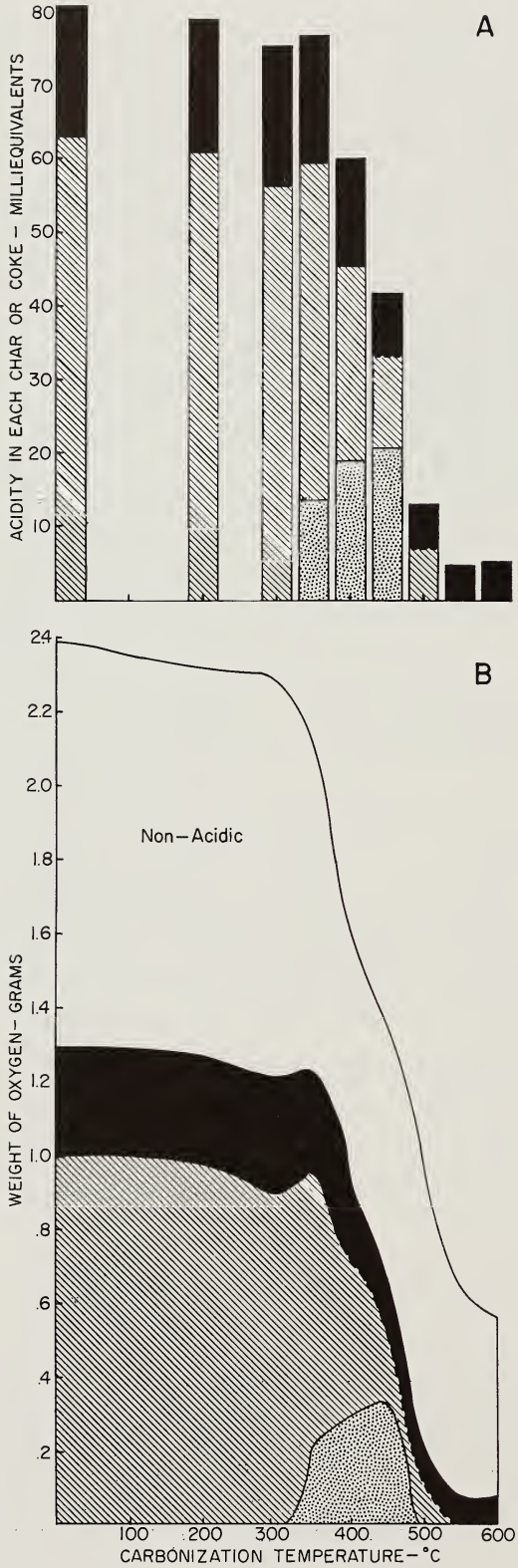


FIG. 12.—Sample N, naturally oxidized coal carbonization series: Titration curves and derived graphs.

The total oxygen decreased from 300°C at a fast rate which was greatest and fairly constant from 350°C to 450°C.

The weight of acidic oxygen decreased slightly to 300°C and then rose by a small amount to 350°C due to the appearance of the new weaker acidity at that temperature. It decreased rapidly between 350°C and 450°C and faster still between 450°C and 500°C with the disappearance of the weakest component acidity. A small amount of this acidic oxygen was apparently con-



verted to a non-acidic form in this range.

The percentage of oxygen in acidic form was highest in the solid carbonization product at 400°C.

Forced Oxidized Coal

Variation of Acidic Groups During Oxidation

At first difficulty was experienced in the titration of the forced oxidized coal. The sample became sticky in ethylenediamine and adhered to the bottom of the flask. It was found that 10 ml of benzene added before the ethylenediamine gave a homogeneous suspension which titrated satisfactorily. The blank also was determined with added benzene in this case.

Table 9 shows that the total acidity increased from 3.78 to 5.37 milliequivalents per gram over the 47 days.

The stronger component acidity increased to more than twice its original value of 0.65 milliequivalents per gram in 17 days, showed a slight further increase after 35 days, and finally after 47 days had risen to more than three times its original value. No new inflection was detected in the titration curve (compare with forced oxidized coal Sample M).

The weaker component acidity showed a small decrease after 17 days, a larger increase in the next 17 days, and again a decrease in the final 12 days to give a net increase of 0.16 milliequivalents per gram over the complete period.

Although this behavior appeared irregular it was noted that the weaker component acidity of Sample M varied in a somewhat similar manner during forced oxidation.

Carbonization

The analytical data for the carbonization series are given in table 25.

Fig. 13.—Sample N, naturally oxidized coal carbonization series:

A. Milliequivalents of total and component acidities in each char or coke.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

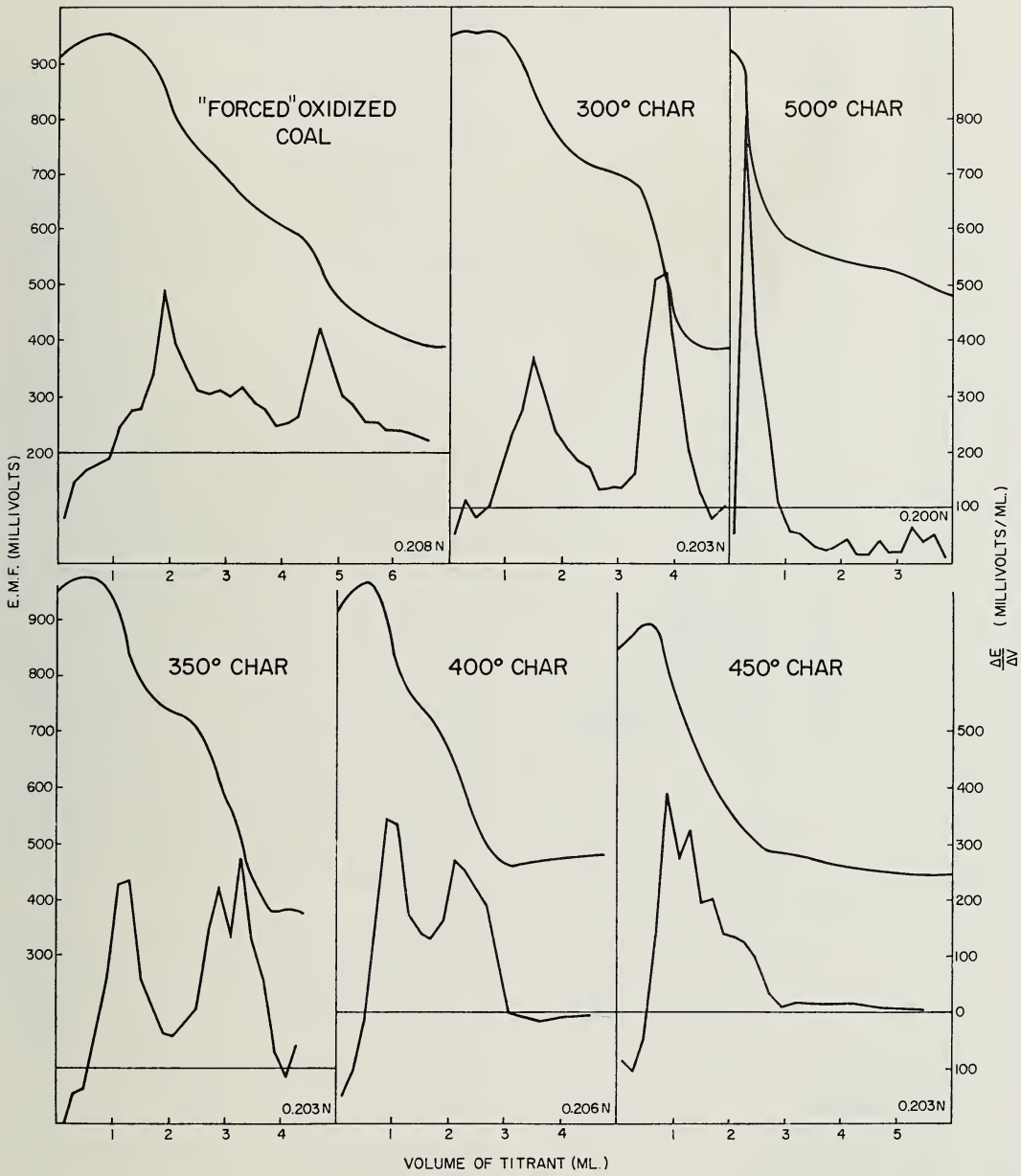
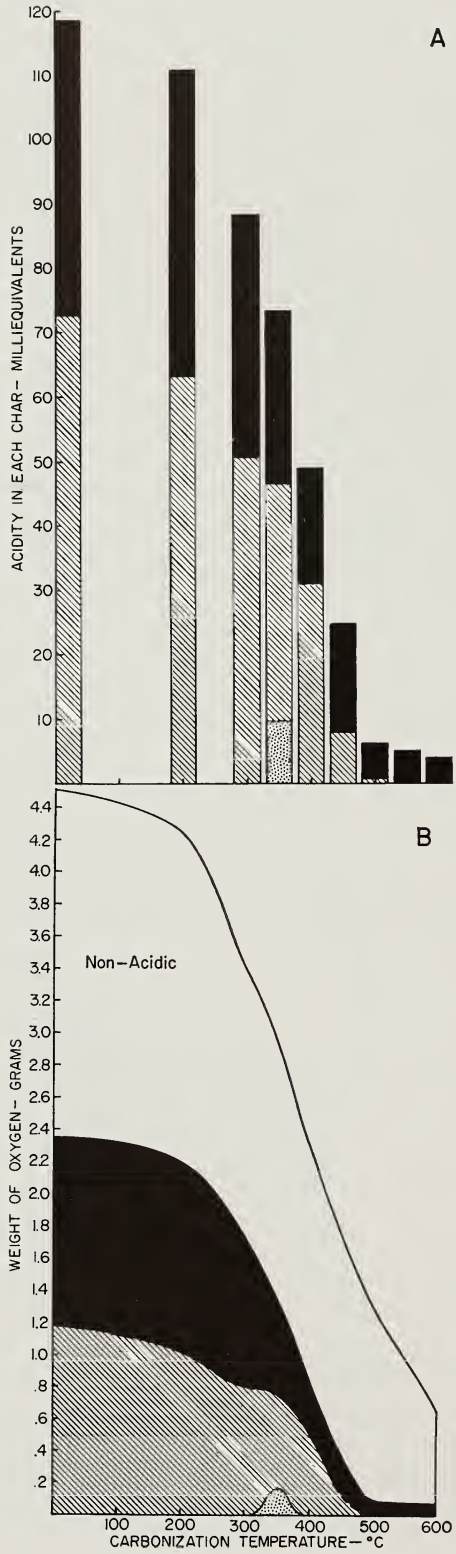


FIG. 14.—Sample N, forced oxidized coal carbonization series: Titration curves and derived graphs.

The oxygen content of the oxidized coal was about twice that of the fresh coal. Up to 550°C in the carbonization series the oxygen content was always significantly greater than for the fresh coal product at the same temperature. Thus it would appear that an appreciable proportion of the oxygen absorbed was in groups that were fairly stable to heat.

The oxidized coal showed a small decrease in volatile matter (38.4 to 36.3 percent) and a large decrease in calorific value (14,452 to 11,923 Btu per pound, or 8029 to 6624 calories per gram) from that of



fresh coal. It had lost all swelling properties and the Gieseler plasticity was unobtainable.

Unconsolidated chars were obtained upon carbonization.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the forced oxidized coal carbonization series is shown in figure 14.

The total acidity and component acidities at each stage of the carbonization are given in table 10. Carboxyl groups formed in the oxidation could not be differentiated in titration from the stronger groups of the type present in the fresh coal, as was possible for coal Sample M. For the purpose of calculating an approximate figure for acidic oxygen these original groups were assumed to be present up to 400°C in the same amount as in the naturally oxidized coal carbonization series. One atom of oxygen per equivalent was assumed for them and for the groups of weaker acidic strength. The remainder of the stronger component acidity was assumed to be due to carboxyl groups and two atoms of oxygen per equivalent was assumed. At 450°C and higher only one atom of oxygen per equivalent was allowed. These estimated acidic oxygen figures are also found in table 10.

The oxidized coal itself gave a titration curve with two fairly sharp inflections. Up to 300°C two inflections were still present. The stronger and (particularly) the weaker component acidities corresponding to them had decreased in value.

At 350°C a third inflection appeared in the curve corresponding to weaker groups than those originally present. There was a

FIG. 15.—Sample N, forced oxidized coal carbonization series:

A. Milliequivalents of total and component acidities in each char.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

further decrease in the values of the original two component acidities.

At 400°C two inflections were present and they appeared to correspond to the original two component acidities decreased even further. At 450°C they were still there, the stronger being about the same value, but the weaker having decreased to a very small value.

At 500°C and higher only one inflection was obtained. The corresponding acidity was very small.

Figure 15*a* shows diagrammatically the number of milliequivalents of the component acidities in each char. The variation in the weight of total oxygen and acidic oxygen (based on the assumption stated above) through the carbonization series is shown in figure 15*b*.

The acidic oxygen as a percentage of total oxygen was greatest in the oxidized coal itself and in the 200° char (about 52 percent), and decreased at a progressively faster rate through the series to a small value (7.6 percent) at 500°C. It increased slightly from 500°C to 600°C, no doubt due to loss of non-acidic oxygen in that range. At no stage of the carbonization did acidic oxygen appear to be converted into non-acidic oxygen or vice versa.

Infrared Spectra

The infrared spectra of fresh, naturally oxidized, and forced oxidized coal Sample N and some of the chars and cokes from them are shown in figure 16.

Fresh Coal Series

The broad absorption band due to hydrogen-bonded O-H at about 3400 cm^{-1} decreased and almost vanished between 350° and 400°C as shown by the fluorolube spectra.

There was little if any indication of aromatic C-H absorption just above 3000 cm^{-1}.

Aliphatic C-H absorption of medium strength was found at 2900 cm^{-1} with a shoulder at 2830 cm^{-1} (slightly higher in fluorolube spectra). It decreased markedly between 350° and 400°C, was almost gone at 450°C, but there was still a suggestion of its presence up to 600°C.

No carbonyl absorption was found in the 1700 cm^{-1} region.

The strong band at 1610 cm^{-1} persisted throughout the series.

The medium strength band due to aliphatic CH_2 and CH_3 at 1440 cm^{-1} decreased above 350°C and was almost gone at 450°C.

Very weak absorption at 1370 cm^{-1}, indicating CH_3 or cyclic CH_2 groups, persisted to 400°C, but seemed to have disappeared at 450°C.

A weak band at 1030 cm^{-1} possibly due to -C-O and/or -C-O-C- seemed to increase in intensity at 350° and 400°C and then decrease to 500°C after which it could no longer be distinguished. Alternatively it may have been caused by silicate or other mineral matter. No definite assignment could be made for any other absorption bands.

Naturally Oxidized Coal Series

The spectrum of the naturally oxidized coal was very similar to that of the fresh coal.

There was no carbonyl absorption at about 1700 cm^{-1}, indicating that no significant numbers of carboxyl groups were formed in the oxidation.

Hydroxyl absorption at 3400 cm^{-1} did not seem to be as strong as in the fresh coal. It showed its greatest decrease between 300° and 400°C although there was still evidence of it at 450°C.

Aliphatic C-H at 2900 cm^{-1} with a shoulder at 2830 cm^{-1} also appeared less strong. It decreased from 300°C and was hardly perceptible at 450°C and higher temperatures.

The band at 1440 cm^{-1} due to aliphatic CH_2 and CH_3 groups also appeared weaker. It disappeared between 350° and 400°C.

The 1030 cm^{-1} band (silicate and/or -C-O-C-, etc.) disappeared between 450° and 500° C. It did not increase at 350° and 400° as it had for the fresh coal.

Forced Oxidized Coal Series

Carbonyl absorption was indicated by a shoulder at 1675-1700 cm^{-1} on the strong 1600 cm^{-1} band up to 400°C.

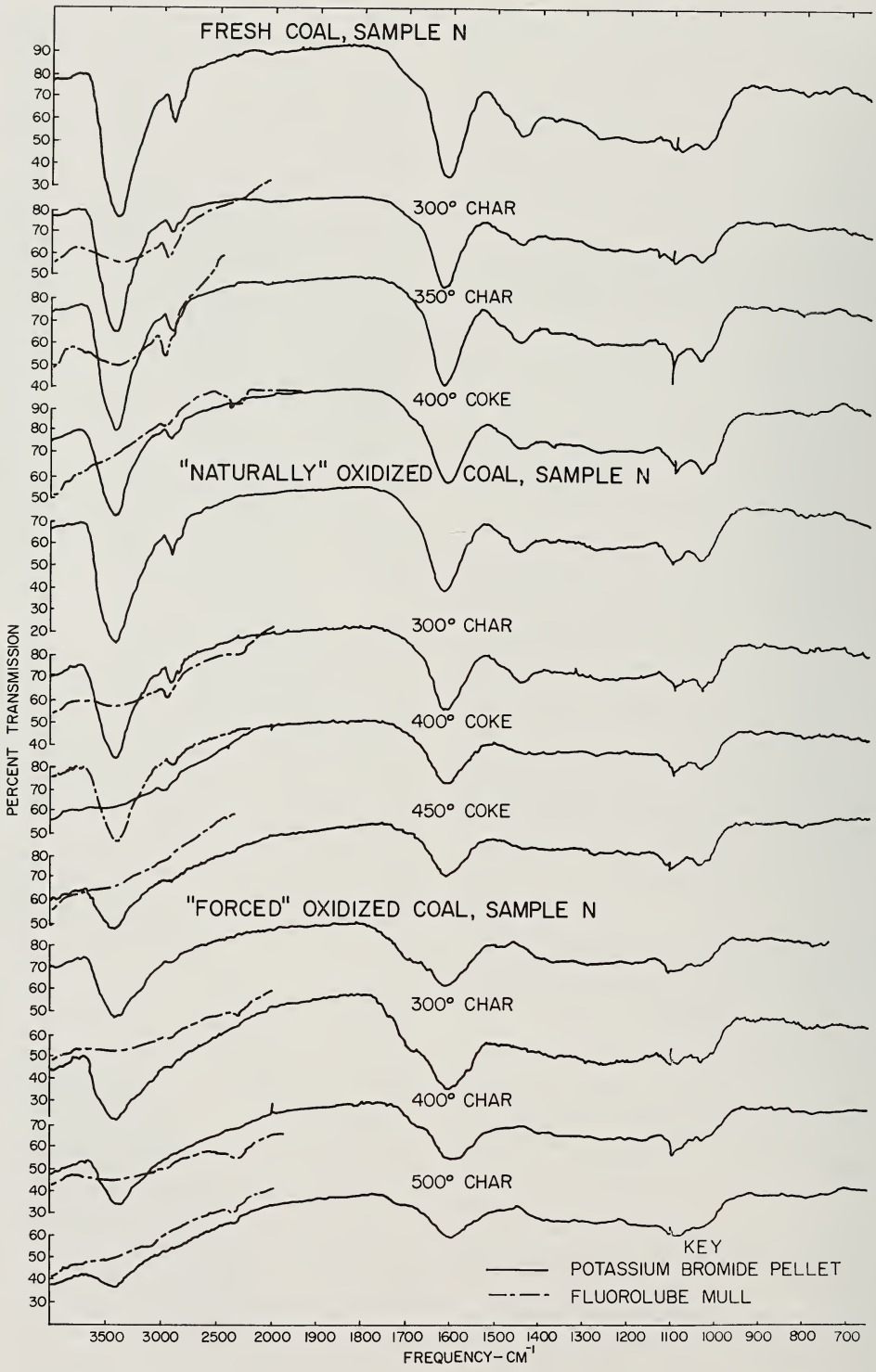


FIG. 16.—Sample N, infrared spectra of the fresh and oxidized coals and some chars and cokes from them.

Once again carboxyl groups appeared to be formed at the expense of aliphatic and naphthenic CH_2 groups. The 2900 cm^{-1} band was very weak and it was difficult to see any 1440 cm^{-1} absorption at all.

The hydrogen-bonded O-H absorption in the 3400 cm^{-1} region was broad, but not very intense. Most of it appeared to have been lost by 500°C in the carbonization series.

SAMPLE O, NO. 5 COAL FROM GALLATIN COUNTY, ILLINOIS

Sample O was a high-volatile A bituminous coal from the No. 5 Coal in Gallatin County, Illinois. It was obtained from a slope mine in the side of a valley; the working face was well underground.

Fresh Coal

The analytical data for the carbonization series of fresh Sample O are given in table 26.

The carbon content (83.17 percent) was higher and the oxygen (7.52 percent) lower than for either Sample M or N. The ash (4.7 percent) was fairly low and the sulfur moderately high (2.18 percent), most (1.84 percent) being organic. The percentage of vitrinite was relatively low (80.5 percent) and of inertinite rather high (10.2 percent).

Carbonization

The free swelling index was fairly high (7) but the Gieseler maximum fluidity unfortunately could not be measured because most of the coal swelled out of the cup and into the barrel. There was a large plastic range (390° to 476°).

At 400°C and above the carbonization products were frothy, very highly swollen cokes.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the fresh coal carbonization series is shown in figure 17.

The total acidity and component acidities at each carbonization temperature are given in table 11, which also gives the total oxygen and acidic oxygen.

The coal itself gave a smooth curve with two fairly sharp inflections. The total acidity was markedly less than for coal Samples M and N. This is in keeping with the coal's higher rank. However, most of the difference was in the weaker component acidity as the stronger was about the same value as that of coal Sample N.

Up to 350°C the form of the titration curve remained the same with two inflections. The total acidity increased by a small amount to 200°C and then decreased gradually to 350°C. The stronger component acidity remained unchanged at 200°C, decreased somewhat at 300°C, and increased again to its original value at 350°C. The weaker component acidity remained fairly constant to 300°C and then decreased by 0.3 milliequivalents per gram to 350°C.

The reproducibility of results obtained with the 400°C coke was not very good. There appeared to be up to four component acidities which could not always be differentiated. For this reason the weaker ones were grouped together in calculating the mean. The total and stronger component acidities showed increases over the 350°C values. The weaker component acidity was about the same as at 350°C, but rather uncertain.

At 450°C two inflections appeared in the curve, but again the reproducibility was not good. The stronger component acidity was slightly less than the 400°C value, but the weaker was only half of the former value. The small inflection seen at 2.5 ml was a non-reproducible irregularity.

At 500°C and above only one inflection, corresponding to a small acidity, was obtained.

Figure 18*a* shows diagrammatically the number of milliequivalents of the component acidities in each char or coke.

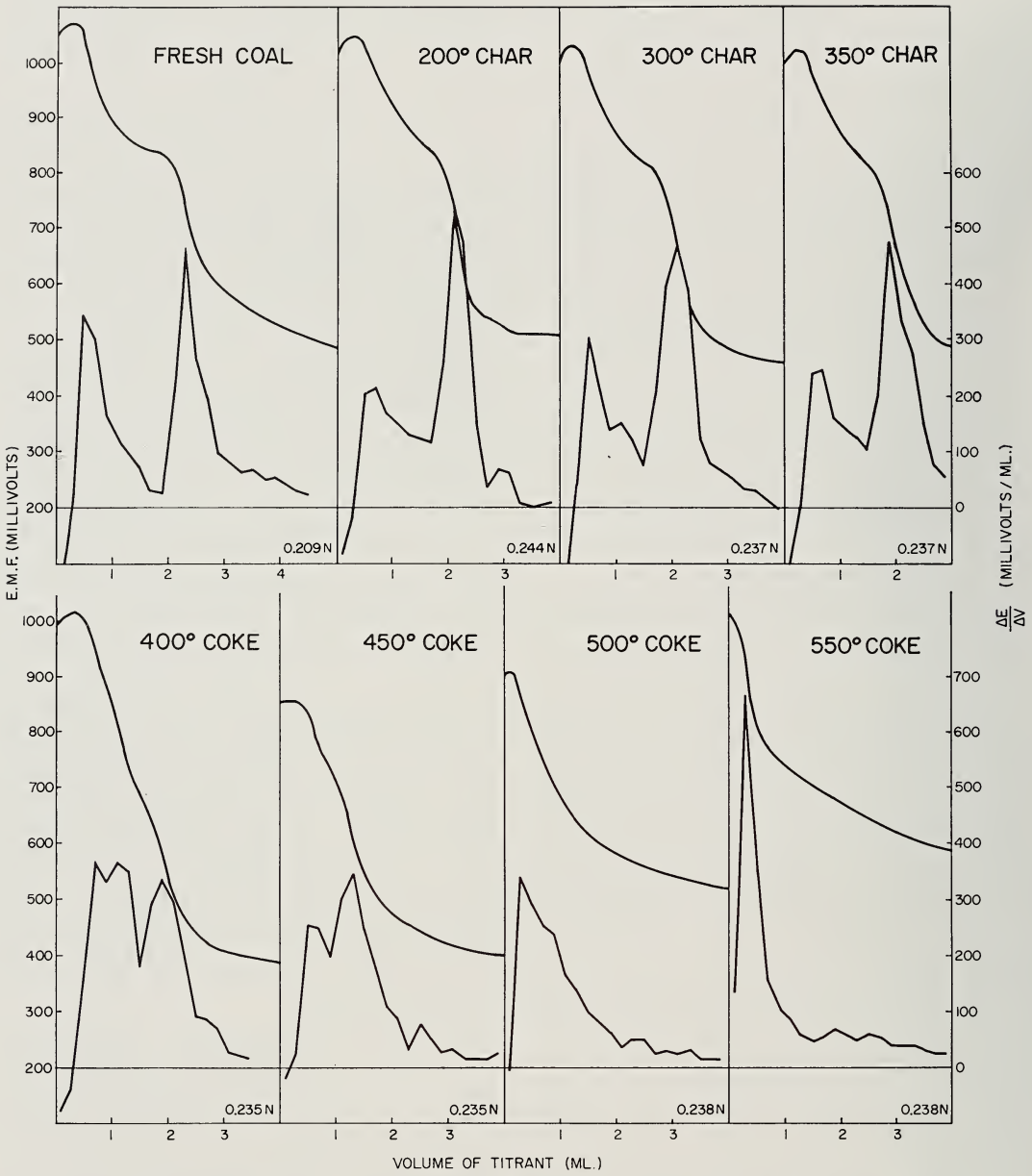


FIG. 17.—Sample O, fresh coal carbonization series: Titration curves and derived graphs.

The variation in the weight of total oxygen and acidic oxygen throughout the carbonization series is shown in figure 18*b*.

The total oxygen decreased rapidly from 350° to 600°C, the fastest rate being from 350° to 400°C.

The acidic oxygen decreased from 200° to 500°C, the rate being greatest between 450° and 500°C. Non-acidic oxygen increased at the expense of acidic in this range.

The percentage of oxygen in acidic form was greatest at 400°C (56 percent) where it was a little higher than in the coal itself.

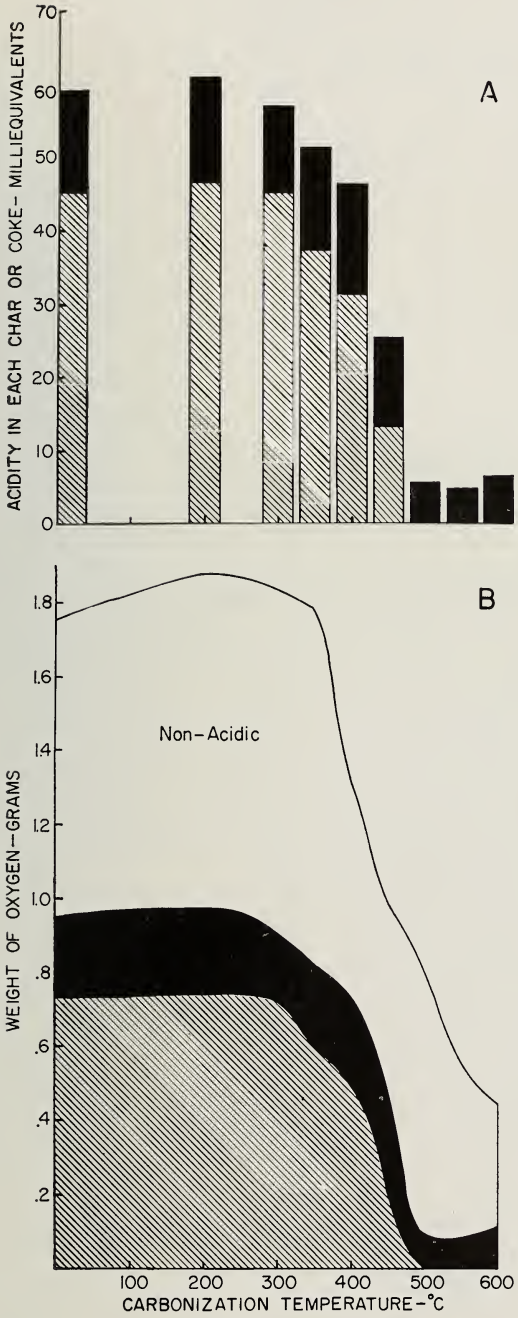


FIG. 18.—Sample O, fresh coal carbonization series:

A. Milliequivalents of total and component acidities in each char or coke.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

NATURALLY OXIDIZED COAL

Variation of Acidic Groups During Oxidation

As shown in table 12 there was a drop in total acidity up to 21 days, followed by rather irregular behavior. After 48 days, three inflections were obtained in the titration curve. After 64 days, the oxidized coal gave a smooth titration curve with two inflections; the total acidity was slightly greater than that of the fresh coal, the increase being in the stronger component acidity.

Carbonization

The analytical data are given in table 27.

The oxygen content of the oxidized coal was only slightly higher than that of the fresh coal. The volatile matter was unchanged, the calorific value showed a small decrease (15,053 to 14,761 Btu per pound or 8,363 to 8,200 calories per gram), the free swelling index had increased by one unit, but the Gieseler plasticity was unobtainable because of high swelling.

The chars and cokes obtained on carbonization were very similar to those from the fresh coal.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the naturally oxidized coal carbonization series for naturally oxidized Sample O is shown in figure 19.

The total acidity and component acidities at each carbonization temperature are given in table 13 which also gives the percentage contents of total and acidic oxygen.

Up to 350°C the form of the curve remained the same. There was a small decrease in the weaker component acidity.

A third inflection was obtained at 400°C. The total acidity was slightly greater than at 350°C although the two component acidities originally present had both decreased in value.

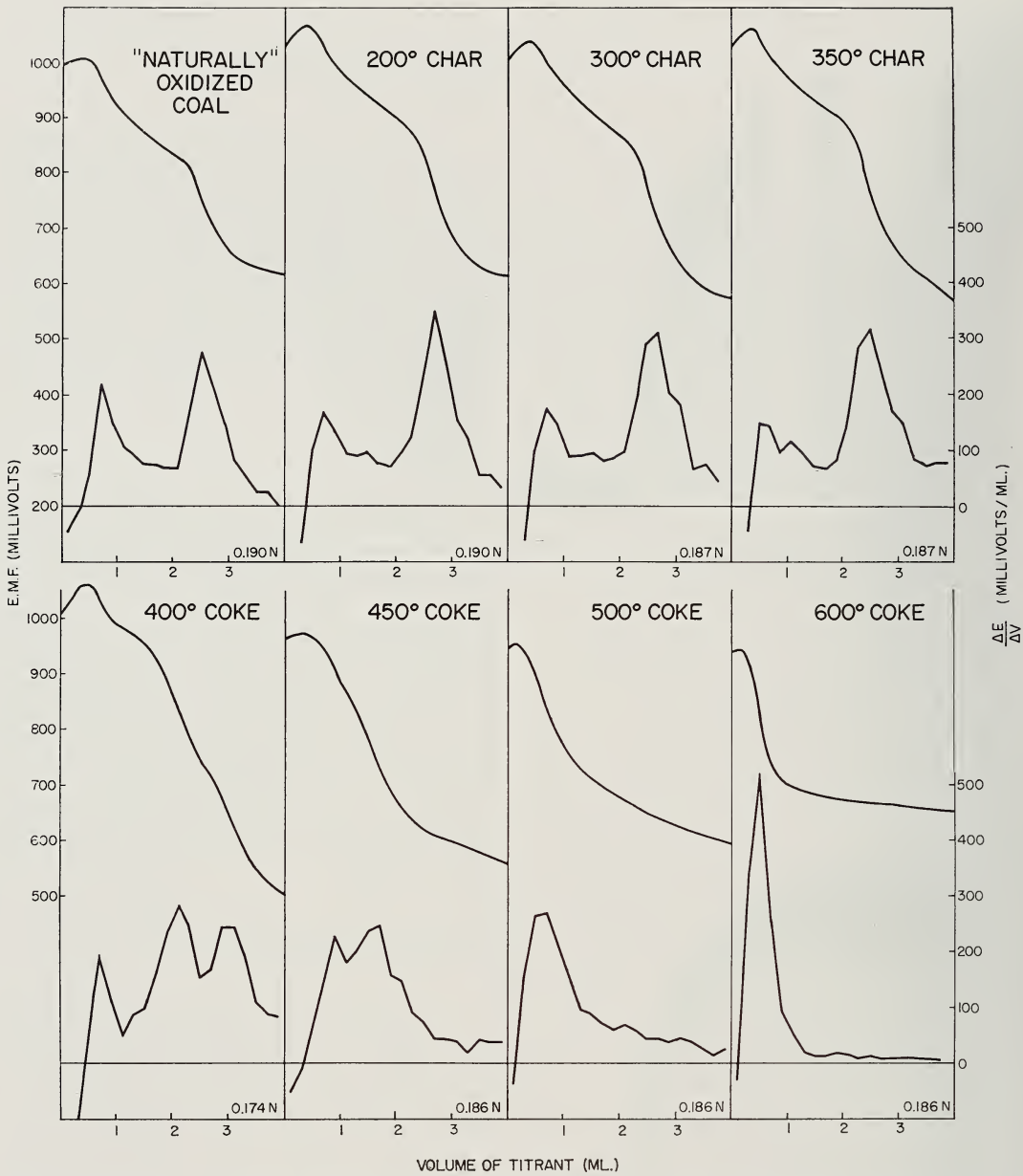


Fig. 19.—Sample O, naturally oxidized coal carbonization series: Titration curves and derived graphs.

At 450°C only two inflections appeared. The total break in the curve was less than at 400°C. The weaker component acidity appeared to correspond with the weakest at 400°C and the stronger seemed to have come from the strongest and second strongest at 400°C.

At 500°C and above only one inflection was obtained. The acidity appeared to correspond with what was left of the stronger at 450°C.

Figure 20*a* shows diagrammatically the number of milliequivalents of the component acidities in each char or coke.

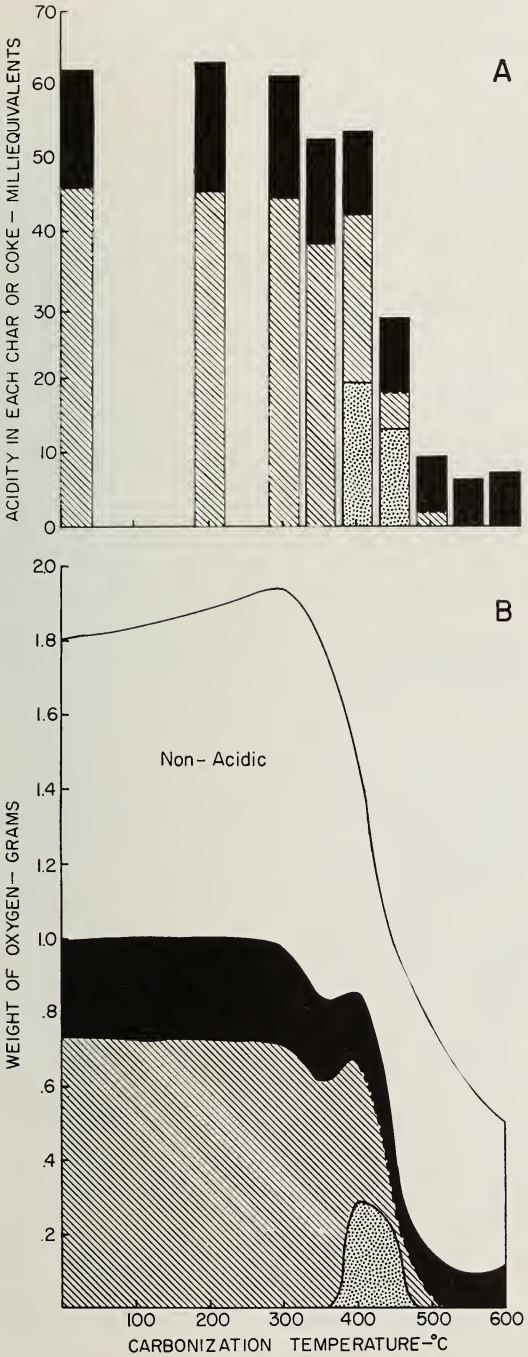


FIG. 20.—Sample O, naturally oxidized coal carbonization series:

A. Milliequivalents of total and component acidities in each char or coke.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

The variation in the weight of total and acidic oxygen throughout the carbonization series is shown in figure 20*b*. The weight of total oxygen fell from 300° to 600°C, the rate being greatest between 400° and 450°C. The weight of acidic oxygen decreased between 300° and 350°C and then rose slightly to 400°C with the appearance of the weakest acidic groups. From there it fell sharply to a low value at 500°C. Some appeared to be converted into a non-acidic form between 450° and 500°C.

The percentage of oxygen in acidic form was at a maximum at 400°C (58 percent), where it was a little higher than in the coal itself.

Forced Oxidized Coal

Variation of Acidic Groups During Oxidation

As shown in table 14 the total acidity of Sample O during oxidation increased from 2.54 to 4.47 milliequivalents per gram over the 47-day period. The increase in the first 14 days was more than twice that in the rest of the time. The stronger component acidity had more than doubled in the first two weeks, trebled after 27 days, and continued to increase more slowly after that. The weaker component acidity increased by about one third in the first 14 days and then remained fairly constant to 36 days before decreasing by a small amount in the final 11 days.

Carbonization

The analytical data for the carbonization series of forced oxidized Sample O are given in table 28.

The oxygen content of the oxidized coal was almost two and a half times that of the fresh coal.

Throughout the series the oxygen content was always markedly greater than for the fresh coal product at the same temperature.

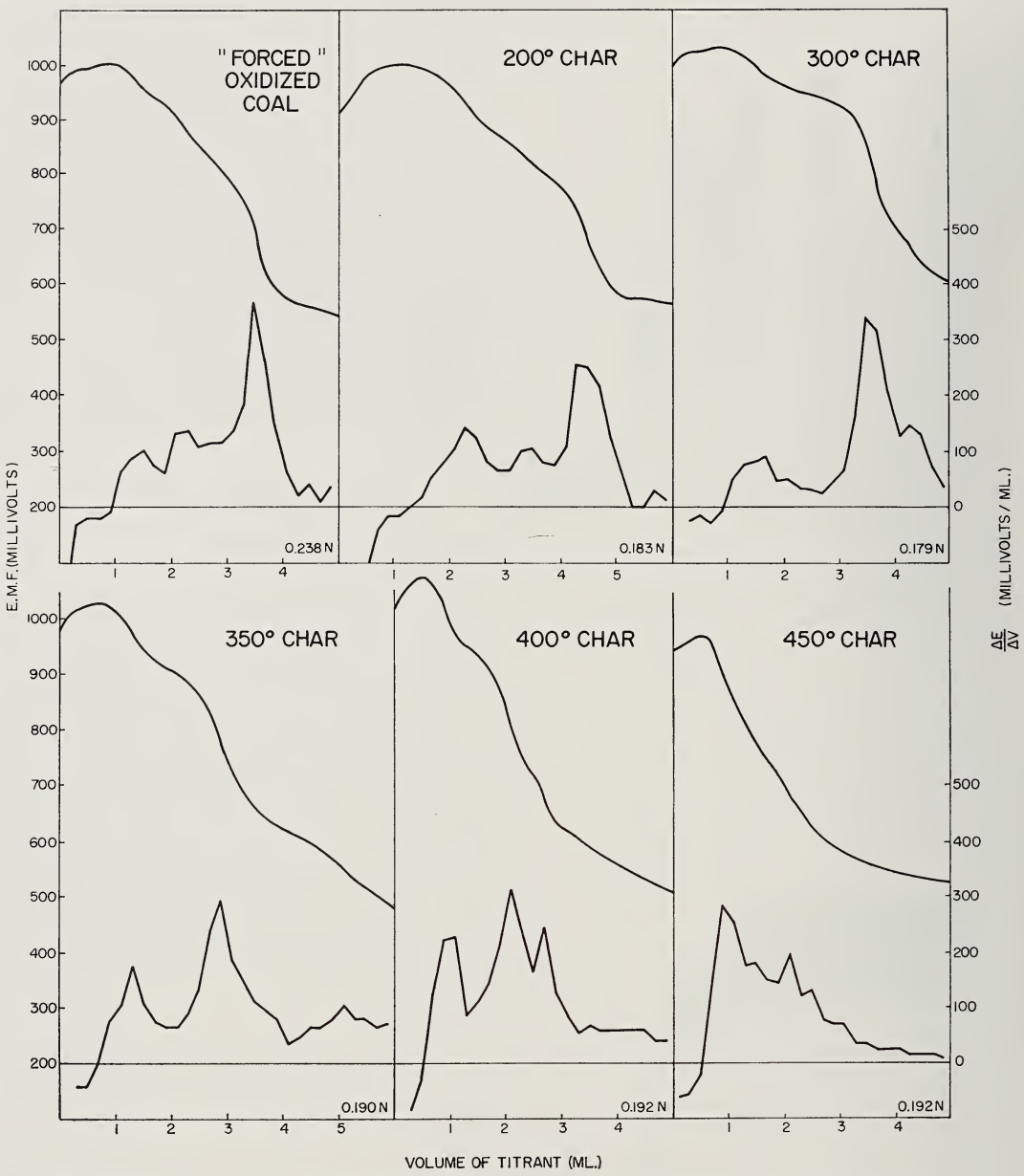


Fig. 21.—Sample O, forced oxidized coal carbonization series: Titration curves and derived graphs.

The oxidized coal showed a decrease in volatile matter (42.5 to 35.7 percent) and a large decrease in calorific value (15,053 to 12,314 Btu per pound or 8363 to 6841 calories per gram) from that of the fresh coal. It had lost all measurable swelling and plastic properties.

The solid carbonization products were unconsolidated chars.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the forced oxidized coal carbonization series is shown in figure 21.

The total acidity and component acidities at each stage of the carbonization are given in table 15.

For the oxidized coal itself there were three inflections in the titration curve in three titrations out of four. The position of the middle one was not very reproducible, so for the mean this inflection was ignored and only a stronger and weaker component acidity given. Carboxyl groups formed in the oxidation are believed to account for part of the stronger component acidity, the remainder being due to groups of the type which give rise to such acidity in the fresh coal.

At 200°C the middle inflection was weak or absent, so only two component acidities were considered. The stronger had increased slightly but the weaker showed a definite decrease.

At 300°C the stronger component acidity had decreased markedly, the weaker by a small amount, and there was a new faint inflection indicating the presence of very weakly acidic groups.

The component acidity due to these extremely weak groups had increased threefold at 350°C. The original two component acidities had decreased by small amounts. The total acidity was higher than in the coal itself.

At 400°C three inflections were once again obtained in the titration curve, but the component acidities had all decreased, particularly that due to the very weak groups. The total acidity was only about half that at 350°C.

Only two inflections were obtained at 450°C, the second being rather faint. These appeared to correspond to the first two inflections at 400°C.

At 500°C and above only one inflection, corresponding to small acidity, was obtained in the titration curve.

For the calculation of acidic oxygen, carboxyl groups were assumed to be responsible for the strongest component acidity in excess of that found in the naturally oxidized series for carbonization products obtained up to 400°C. Infrared spectra indicated their presence up to that temperature. Two oxygen atoms per equivalent were assumed for such groups and one per equivalent for the remainder. Figure 22*a* shows diagrammatically the number of milliequivalents of the component acidities in each char.

The variation in the weight of total oxygen and acidic oxygen (based on the assumption stated above) through the carbonization series is shown in figure 22*b*.

The acidic oxygen as a percentage of total oxygen was greatest at 350°C (70 percent) due to the presence of the extremely weak groups at that temperature.

Between 300° and 350°C acidic oxygen increased at the expense of non-acidic, but between 350° and 400°C the reverse was true.

Infrared Spectra

The infrared spectra of fresh, naturally oxidized, and forced oxidized coal Sample O and some of the chars and cokes from them are shown in figure 23.

Fresh Coal Series

Very broad absorption due to hydrogen-bonded O-H (and N-H?) groups was seen up to 350°C. The flat "peak" was at about 3400 cm^{-1}.

A small number of aromatic C-H groups was indicated by a very faint absorption peak at about 3050 cm^{-1} up to 500°C.

Aliphatic and/or naphthenic C-H absorption of medium strength was found at 2930 cm^{-1} with a shoulder at 2870 cm^{-1} up to 350°C. It was very weak at 400°C and could not be seen at higher temperatures.

No C:O absorption was found in the 1700 cm^{-1} region.

The strong and broad 1600 cm^{-1} band persisted throughout the series.

The medium strength band due to aliphatic and/or naphthenic CH_2 and CH_3 groups at 1440 cm^{-1} decreased between 350° and 400°C, and at 450°C and above could not be distinguished from the general absorption.

The weak peak at 1370 cm^{-1} due to CH_3 or cyclic CH_2 groups could not be seen above 400°C.

The broad absorption from 1200 to 1000 cm^{-1}, particularly noticeable in the 500°, 550°, and 600°C cokes, may have indicated aromatic ethers, but may also have been largely due to mineral matter.

The weak peak at 1030 cm^{-1} likewise may have been caused by ethers and/or kaolinite. It could be distinguished up to 450°C.

Naturally Oxidized Coal Series

The broad hydrogen-bonded O-H absorption at about 3400 cm^{-1} decreased between 300° and 350°C. It could not be seen after 400°C.

Slight aromatic C-H absorption could be distinguished at least up to 400°C at about 3060 cm^{-1}.

Medium strength aliphatic and/or naphthenic C-H absorption decreased above 300°C, but was still evident up to 450°C. It occurred at about 2940 cm^{-1} with a shoulder at about 2880 cm^{-1}.

The strong broad band with its peak from 1620 to 1605 cm^{-1} persisted throughout the series.

The band of medium strength with peak at 1450 - 1440 cm^{-1} due to CH_2 and CH_3 groups decreased gradually to 400°C. It may have still been present at 450°C, but was gone at higher temperatures.

The weak band at 1375 cm^{-1} due to CH_3 and cyclic CH_2 groups persisted to 400°C after which its presence was uncertain.

The bands in the 1200 to 1000 cm^{-1} region, which merged into general absorption at higher temperatures, were most probably due to aromatic C-O structures (e.g., ethers) with interference from mineral matter.

The three very weak bands at about 860, 810, and 750 cm^{-1} may have been due to variously substituted benzene structures.

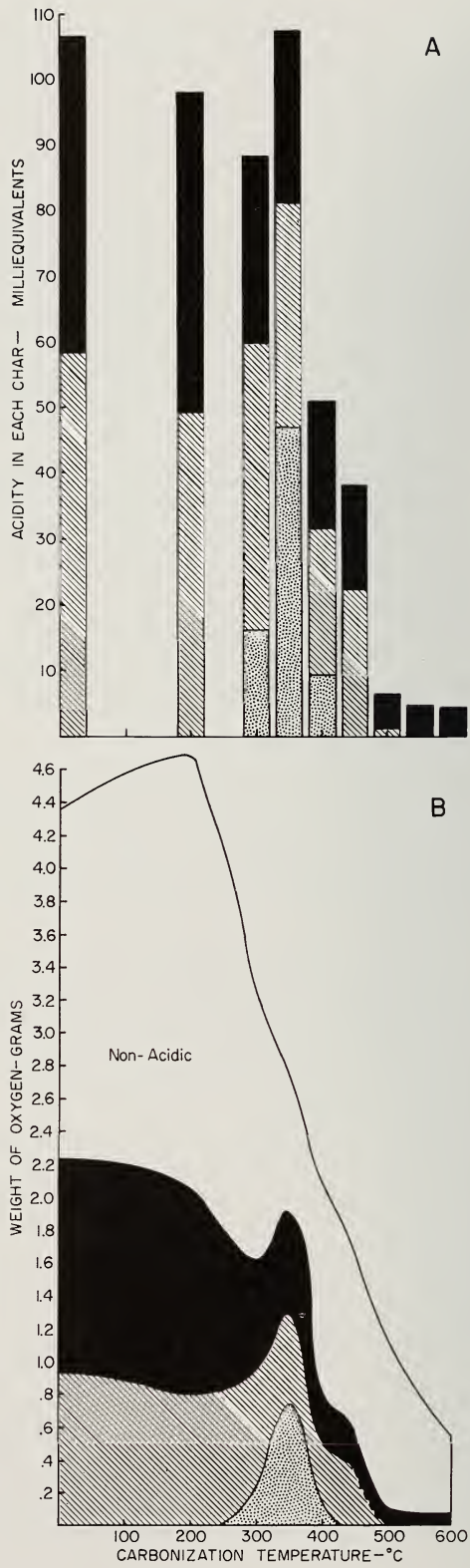


FIG. 22.—Sample O, forced oxidized coal carbonization series:

A. Milliequivalents of total and component acidities in each char.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

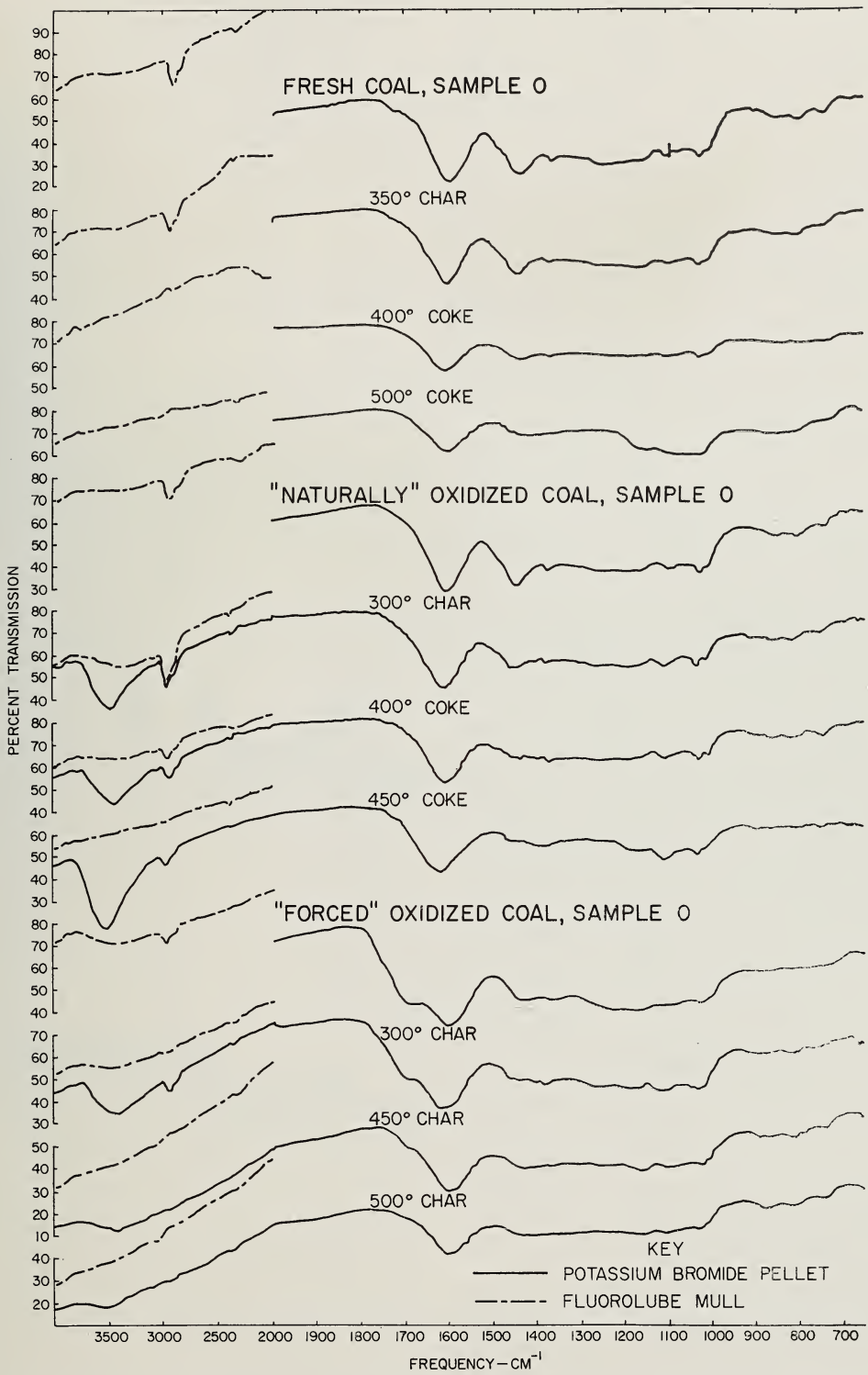


FIG. 23.—Sample O, infrared spectra of the fresh and oxidized coals and some chars and cokes from them.

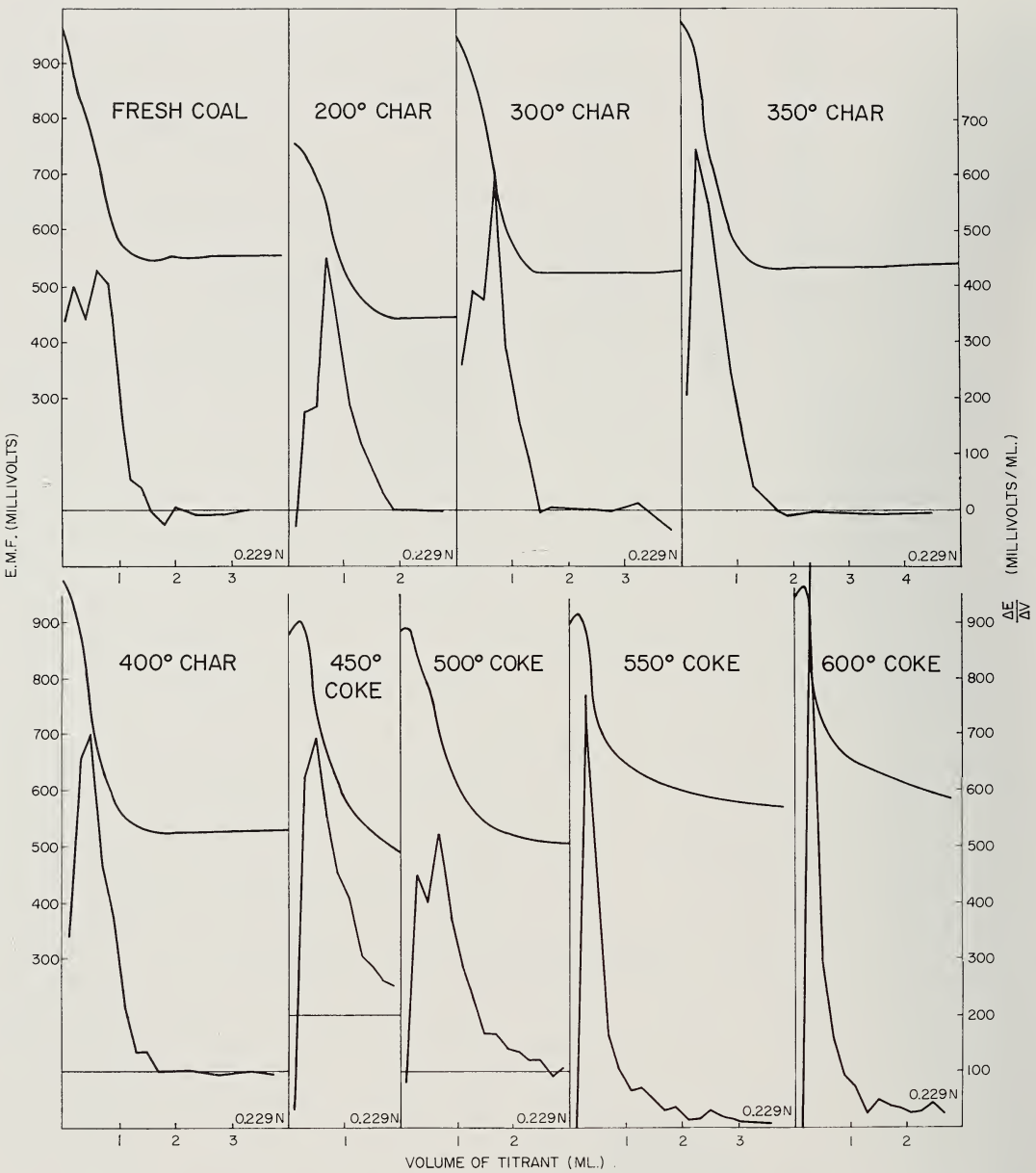


Fig. 24.—Sample P, fresh coal carbonization series: Titration curves and derived graphs.

The 750 cm^{-1} band was seen up to 600°C, the others to at least 400°C.

Forced Oxidized Coal Series

The spectra showed a very strong shoulder at 1700 cm^{-1} on the 1600 cm^{-1} band due to C:O in carboxyl groups formed in the oxidation. The shoulder decreased in intensity above 200°C, being seen last at 450°C where it was very weak.

The bands due to aliphatic and/or naphthenic C-H and CH_2 at 2940 and 1440 cm^{-1} were markedly decreased from those in the spectrum of the naturally oxidized coal.

The behavior of the various other absorption bands with increase of carbonization temperature followed much the same pattern as before.

SAMPLE P, POCAHONTAS COAL FROM McDOWELL COUNTY, WEST VIRGINIA

Sample P was a low-volatile bituminous coal from an underground mine operating in Pocahontas No. 3 seam in McDowell County, West Virginia.

Fresh Coal

The analytical data for the carbonization series of fresh Sample P are given in table 29.

This was a very high rank bituminous coal (91.23 percent carbon) used in the production of metallurgical coke. Both the ash (2.4 percent) and sulfur (0.56 percent) contents were low. Practically all the sulfur was in organic form.

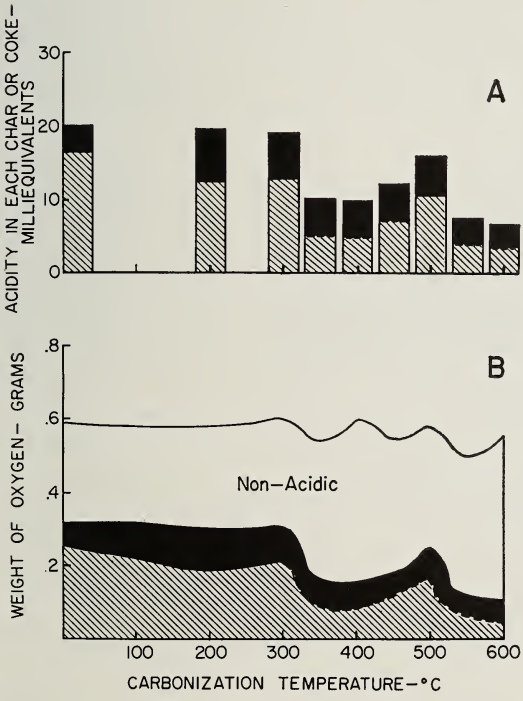


Fig. 25.—Sample P, fresh coal carbonization series:

A Milliequivalents of total and component acidities in each char or coke.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

The percentage of vitrinite was moderate (85.6 percent), inertinite fairly large (13.4 percent) and no exinite was present.

Carbonization

The free swelling index was high (9), but the Gieseler maximum fluidity low (85 dial divisions per minute). The plastic range was very short (459-484°C).

At 450°C and above, highly swollen cokes were obtained but they were moderately hard.

Variation of Acidic Groups During Carbonization

The titration curves and derived graphs from the fresh coal carbonization series are shown in figure 24.

The total acidity and component acidities at each carbonization temperature are given in table 16, which also gives the total oxygen and acidic oxygen.

Up to 300°C the curve showed two inflections which could just be differentiated. The total acidity was very low in comparison with the other coals studied.

The stronger component acidity increased by a small amount to 200°C and then decreased slightly to 300°C. The weaker component acidity decreased by a similar small amount to 200°C and then remained substantially the same at 300°C.

At 350°C, 400°C, and 450°C only one inflection was obtained. The acidity decreased by a small amount to 350°C, remained the same at 400°C and then increased again.

At 500°C two inflections were obtained and the component acidities were very close to those obtained at 300°C.

At 550°C and 600° C only one inflection was found.

Figure 25*a* shows diagrammatically the number of milliequivalents of the component acidities in each char or coke.

The variation in the weight of total oxygen and acidic oxygen throughout the carbonization series is shown in figure 25*b*.

The weight of total oxygen varied in an irregular manner that seemed to indicate

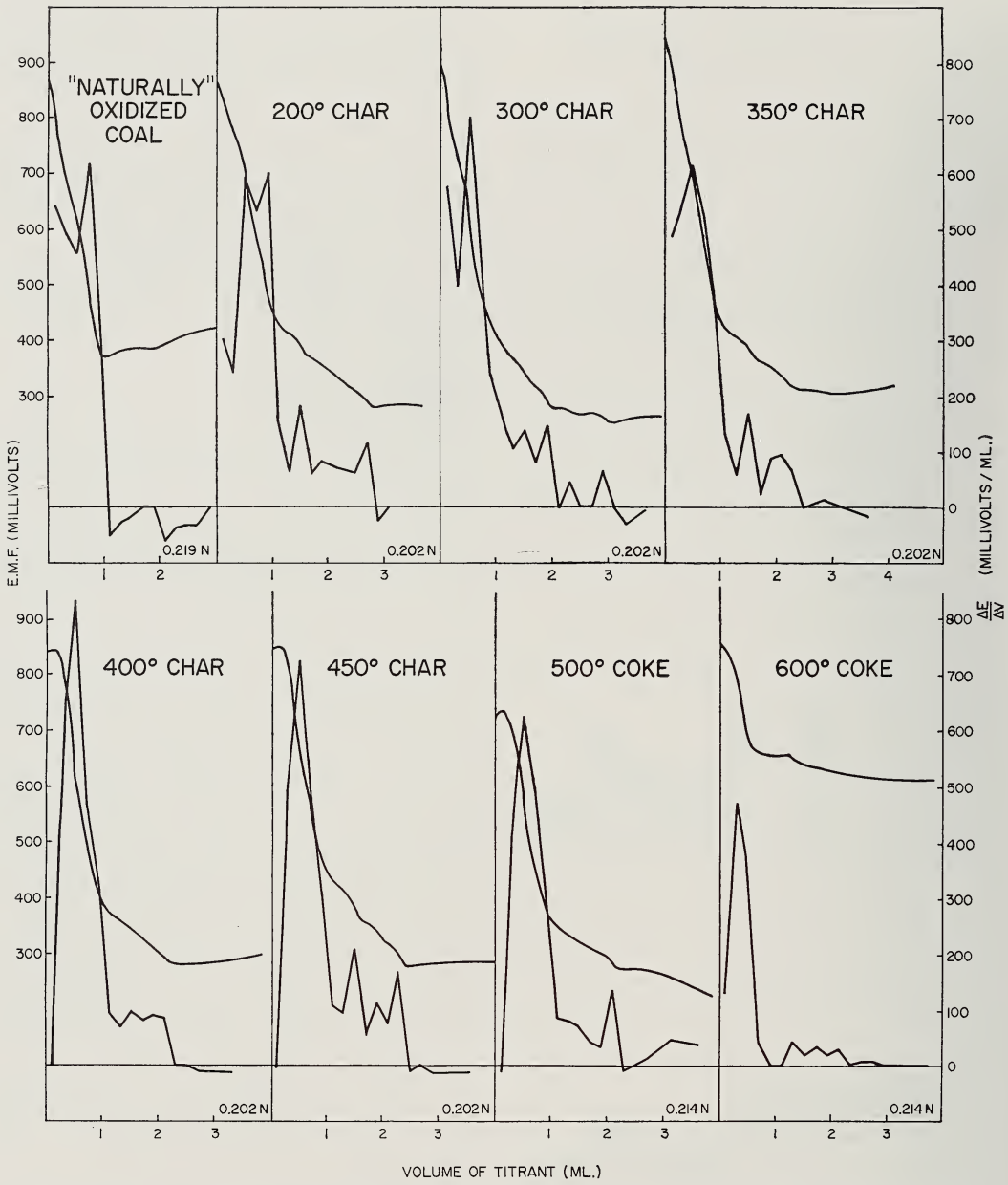


Fig. 26.—Sample P, naturally oxidized coal carbonization series: Titration curves and derived graphs.

error in determination. The inherent error in oxygen content obtained by difference would be greatest in such a low-oxygen coal.

The weight of acidic oxygen decreased slightly to 300°C and then fell suddenly to 350°C with the loss of the stronger component acidity. It was steady to 400°, rose slowly to 450°, then had a small sharp rise to 500°C. It fell off to a very low value at 550° and 600°C.

The percentage of oxygen in acidic form was a maximum in the coal itself (54 percent), decreased to 400°, increased to 450° and 500°C (44 percent) and then fell off to a low proportion.

Naturally Oxidized Coal

Variation of Acidic Groups During Oxidation

The total acidity fell from 0.83 to 0.62 milliequivalents per gram in the 64 days. Both component acidities decreased by small amounts.

Carbonization

The analytical data are given in table 30.

The oxidized coal and the chars and cokes from it apparently had slightly lower oxygen contents than the fresh coal and its corresponding carbonization products. This may have been due to error in the determination of oxygen by difference.

The oxidized coal had slightly higher volatile matter and slightly lower calorific value than the fresh coal, the free swelling index was unchanged, but the Gieseler plasticity had decreased from 85 to 22 dial divisions per minute and the solidification temperature was 504°C whereas originally it was 484°C.

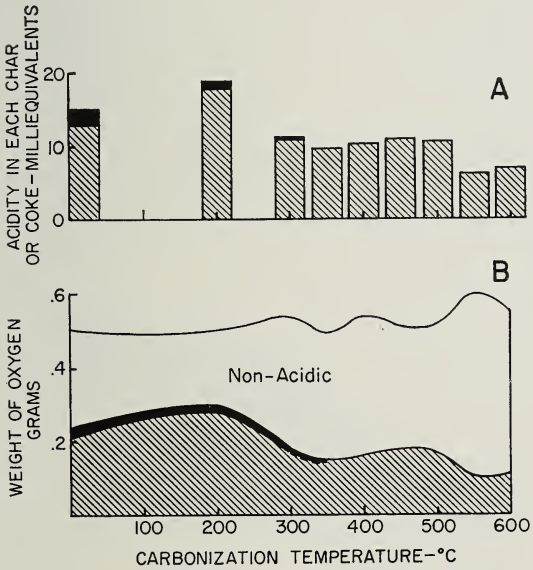


Fig. 27.—Sample P, naturally oxidized coal carbonization series:

A. Milliequivalents of total and component acidities in each char or coke.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

The chars and cokes obtained on carbonization were similar to those from the fresh coal.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the naturally oxidized coal carbonization series is shown in figure 26.

The total acidity and component acidities at each carbonization temperature are given in table 17, which also gives the total oxygen and acidic oxygen.

Up to 300°C the curve showed two inflections which could just be differentiated. When the solvent blank was subtracted the stronger component acidity was found to be very small, decreasing to a negligible quantity at 300°C. At 350°C and above only one inflection was obtained.

The total acidity remained fairly constant from 300° to 500°C and then decreased at 550° and 600°C.

The starting E.M.F. remained fairly high throughout the series. In many cases there were non-reproducible irregularities in the tails of the titration curves.

Figure 27*a* shows diagrammatically the number of milliequivalents of acidity in each char or coke.

The variation in the weight of total oxygen and acidic oxygen throughout the carbonization series is shown in figure 27*b*.

The weight of total oxygen varied in an irregular manner which once again most probably indicated error due to oxygen determination by difference.

The weight of acidic oxygen apparently increased by a small amount to 200°C, fell fairly rapidly to 350°C where the small amount of the stronger component acidity could no longer be differentiated, rose slightly to 500°C and then decreased again to 550 and 600°C.

The percentage of oxygen in acidic form was a maximum in the 200°C char (60 percent), decreased to 400°C (31 percent), increased slightly to 450°C (34 percent) and 500°C (33 percent) and then fell off to about half this proportion at 550° and 600°C.

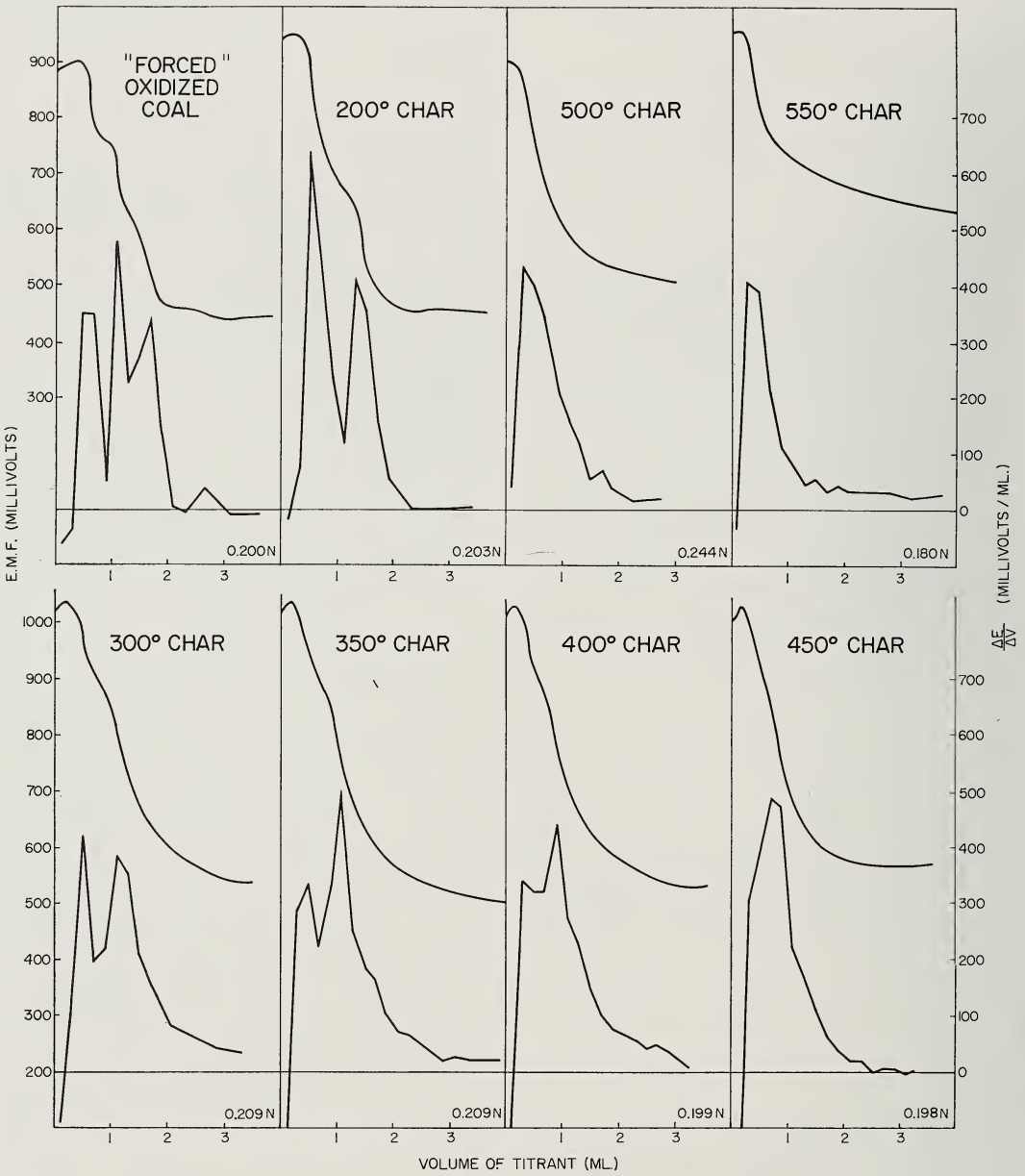


Fig. 28.—Sample P, forced oxidized coal carbonization series: Titration curves and derived graphs.

Forced Oxidized Coal

Variation of Acidic Groups During Oxidation

As shown in table 18 the total acidity increased to almost twice its original value over the 47-day period. However, the increase in the first 37 days was less than in the final ten, perhaps indicating that there was an initial decrease corresponding to natural oxidation.

The stronger component acidity showed a larger percentage increase than the weaker. The latter at the end of the period could be differentiated into two separate component acidities, each of which had almost the same value as the strongest (0.55 milliequivalents per gram).

Carbonization

The analytical data for the carbonization series are given in table 31.

The oxygen content of the oxidized coal was more than twice that of the fresh coal. Up to 450°C in the carbonization series the oxygen content was significantly more than in the fresh coal product at the same temperature.

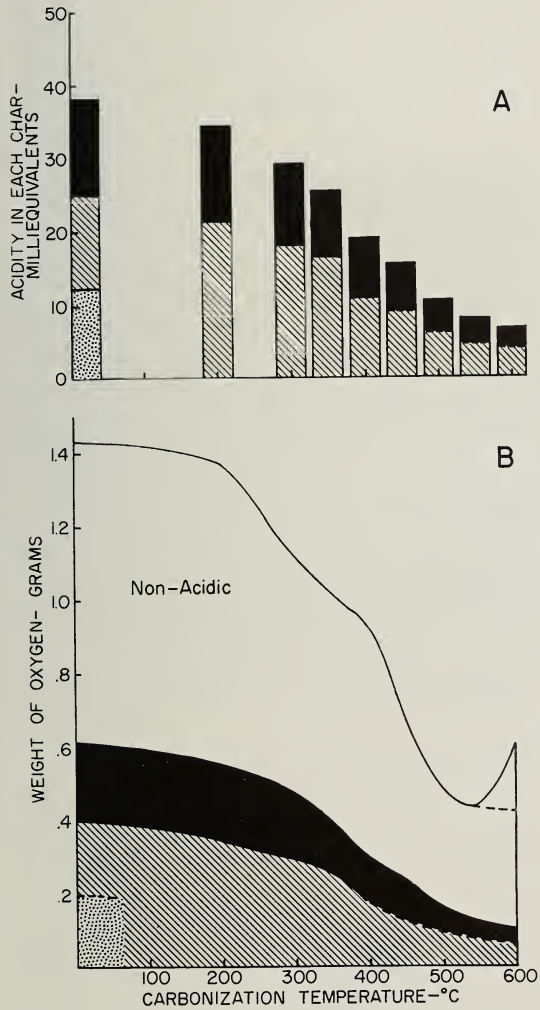


FIG. 29.—Sample P, forced oxidized coal carbonization series:

A. Milliequivalents of total and component acidities in each char.

B. Variation of weight of oxygen (acidic and non-acidic) with carbonization temperature.

Shaded areas represent distinguishable component acidities in order of decreasing acidic strength, the strongest at the top.

The volatile matter was the same as for the fresh coal. The calorific value had decreased (15,647 to 14,933 Btu per pound or 8693 to 8296 calories per gram). The oxidized coal had lost all swelling and agglomerating properties.

Carbonization yielded unconsolidated chars.

Variation of Acidic Groups During Carbonization

A selection of titration curves and derived graphs from the forced oxidized coal carbonization series is shown in figure 28. The total and component acidities are given in table 19, together with total and acidic oxygen.

The coal itself gave a titration curve with three inflections, the corresponding component acidities being roughly equal in magnitude.

From 200° to 400°C two inflections were obtained, the first corresponding to the strongest component acidity in the coal itself, gradually decreasing in value. The second appeared to correspond to what was left of the weaker two in the coal, differentiation being no longer obtained. It decreased slowly to 350°C and more quickly to 400°C.

At 450°C and higher temperatures only one inflection was obtained. The total acidity continued to decrease, but at 450°C was higher than either of the components alone at 400°C, indicating that groups of both strengths were still present, but differentiation was no longer possible.

The percentage of oxygen in acidic form was a maximum in the coal itself (43 percent).

Figure 29*a* shows diagrammatically the number of milliequivalents of the component acidities in each char.

The variation in the weight of total oxygen and acidic oxygen throughout the carbonization series is shown in figure 29*b*. The value for total oxygen at 600°C is obviously too high. This may have been due to error in determination by the difference method or to further oxidation before analysis despite precautions. Since the oxidized coal did not appear to show carbonyl

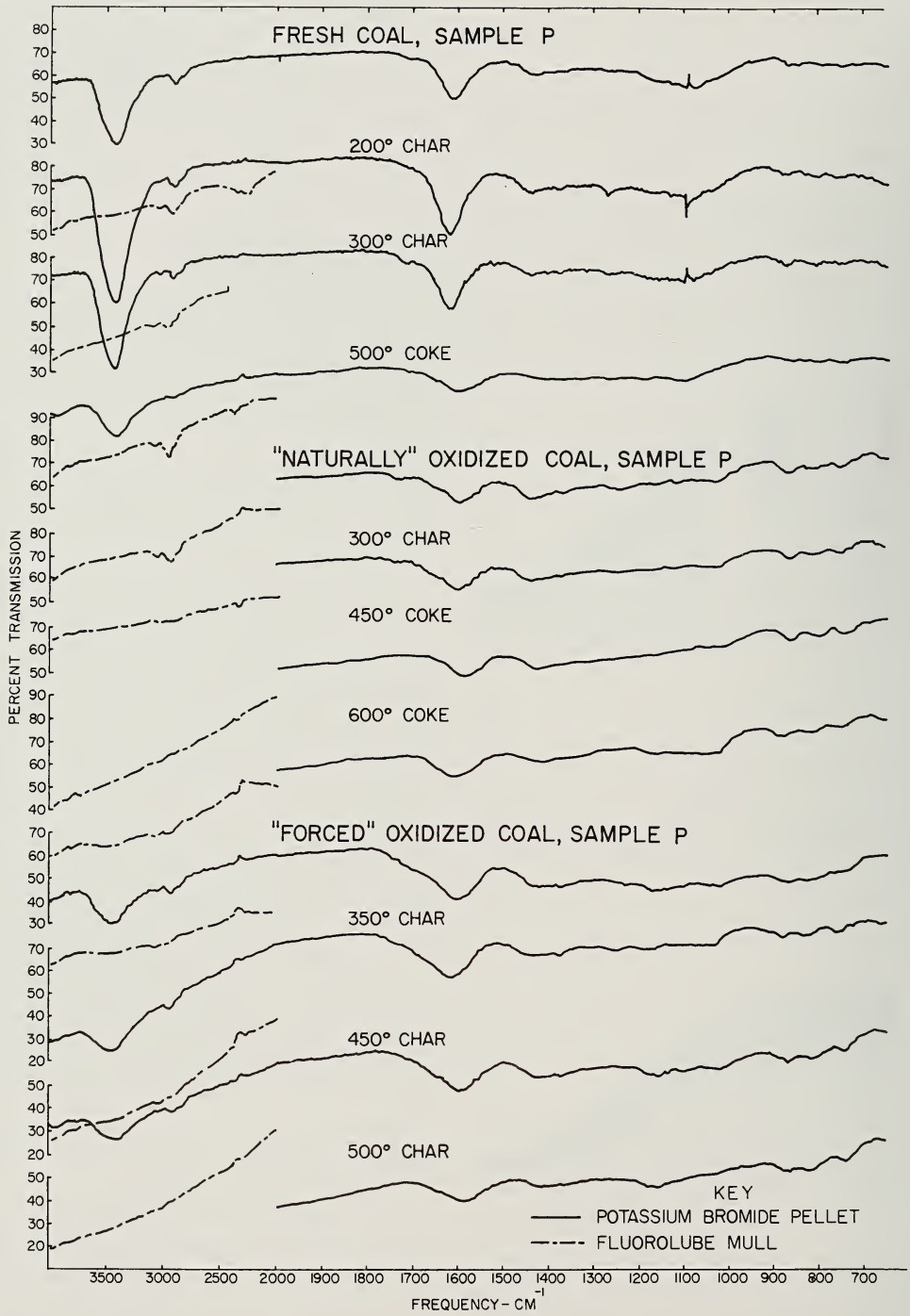


FIG. 30.—Sample P, infrared spectra of the fresh and oxidized coals and some chars and cokes from them.

absorption in its infrared spectrum (at about 1700 cm^{-1}) and exhibited no noticeable solubility in sodium hydroxide solution, it was concluded that carboxyl groups had not been formed to any appreciable extent in the oxidation. Accordingly acidic oxygen was calculated on the basis of one oxygen atom per equivalent of acidity.

Infrared Spectra

The infrared spectra of fresh, naturally oxidized, and forced oxidized coal Sample P and some of the chars and cokes from them are shown in figure 30.

Fresh Coal Series

The hydrogen-bonded O-H absorption at about 3400 cm^{-1} was very weak even at the start of the series, as shown by the fluorolube spectra at 200° and 300°C. That shown by the potassium bromide spectra must have been largely due to water.

Weak absorption due to aromatic C-H appeared at about 3030 cm^{-1} up to 450°C. For some reason it showed up better in the fluorolube spectra than in the potassium bromide spectra.

Aliphatic and/or naphthenic C-H absorption appeared at about 2910 cm^{-1} with a weak shoulder at about 2840 cm^{-1}. It was stronger than the aromatic C-H absorption, but still rather weak. It decreased in intensity between 400° and 450°C but was barely perceptible at 500°C and higher temperatures.

The strong 1615 cm^{-1} band persisted throughout the series with gradually decreasing intensity.

Aliphatic and/or naphthenic CH_2 and CH_3 groups were indicated by medium strength absorption at about 1435 cm^{-1}. They were present to 450°C, but seemed to have been eliminated at 500°C.

An extremely weak peak at 1375 cm^{-1} could be distinguished in most of the spectra up to 450°C. It indicated CH_3 or cyclic CH_2 groups in small numbers.

Three very weak bands at about 865, 795 and 745 cm^{-1} may have indicated benzene rings substituted in different ways. They were most noticeable at 400° and 450°C, could just be distinguished at 500°C, but could no longer be seen at 550° and 600°C.

Naturally Oxidized Coal Series

Little hydrogen-bonded O-H absorption at about 3500 cm^{-1} could be seen even in the coal itself.

Very weak aromatic C-H absorption at about 3060 cm^{-1} decreased above 400°C but even at 600°C a suggestion of it was still apparent.

The aliphatic and/or naphthenic absorption at 2940 cm^{-1} with a shoulder at 2870 cm^{-1} was stronger. It began to decrease from 300°C and could no longer be seen at 500°C.

The "coal band" at about 1600 cm^{-1} persisted throughout the series.

Medium strength absorption at about 1435 cm^{-1} (CH_2 and CH_3 groups) was seen up to 500°C after which it merged with general absorption in the 1450-1350 cm^{-1} region.

A very weak peak at 1370 cm^{-1} (CH_3 or cyclic CH_2) was seen up to 400°C.

The three weak bands indicating substituted benzene structures appeared at about 865, 805, and 750 cm^{-1} and could be seen in all members of the series.

Forced Oxidized Coal Series

Hydrogen-bonded O-H was indicated by broad absorption of low intensity at about 3500 cm^{-1}. It became less noticeable as the temperature increased.

Weak aromatic C-H absorption was seen up to 450°C at 3050 cm^{-1}.

The weak aliphatic and/or naphthenic C-H band at about 2930 cm^{-1} with a shoulder at about 2860 cm^{-1} persisted up to 450°C. For some reason, it was stronger in the potassium bromide spectra than in the fluorolube, where it was only about the same intensity as the aromatic C-H.

There was no appreciable absorption due to C:O at about 1700 cm^{-1} although the 1600 cm^{-1} did seem to be broadened on that side. It would appear that few, if any, carboxyl groups were formed in the oxidation. This is supported by the failure of the oxidized coal to show pronounced caustic solubility.

The strong, broad 1600 cm^{-1} band was seen throughout the series.

The medium strength CH_2 and CH_3 absorption at about 1435 cm^{-1} and the very weak CH_3 or cyclic CH_2 band at about 1375 cm^{-1} were seen up to 500°C where they merged into the general absorption.

The three weak bands from substituted benzene structures were seen at about 870, 815 and 750 cm^{-1} throughout the series.

SAMPLE Q, WILLIS COAL FROM GALLATIN COUNTY, ILLINOIS

Sample Q was a high-volatile A bituminous coal of the Willis seam in Gallatin County, Illinois, and was obtained by Dr. E. D. Pierron of this laboratory for use in another investigation. It was not carried through the oxidation and carbonization series applied to previous coals, but was titrated fresh to get additional data for the comparison of the acidities of coals of various ranks.

This coal is said to be the highest rank coal known in Illinois.

Analytical data are given in table 32. It is a high sulfur coal (3.30 percent), but most of this sulfur (2.52 percent) is pyritic.

Titration Experiments

On titration two inflections were obtained corresponding to a total acidity of 1.96 milliequivalents per gram, made up of a stronger component (0.46 milliequivalents per gram) and a weaker component of 1.50 milliequivalents per gram.

RISE IN E.M.F. BEFORE TITRATION

The initial E.M.F., as soon as the indicator electrode was inserted, was usually about 550 to 600 mv. In many cases it rose steadily to about 700 mv in about 2 to 2½ hours and then rose very quickly to more than 900 millivolts. However, for a number of chars and cokes obtained at 450°C and higher temperatures, this further rise did not take place.

At first it was thought that a delayed action swelling effect might be responsible for the sudden increase in E.M.F., but this was disproved as follows. A sample which was known to show the effect was put into suspension in the ethylenediamine in the titration flask and stirred with a magnet-impelled stirrer overnight. Next morning the flask was fitted to the apparatus and the electrode inserted. The E.M.F. was only 550 mv. However, it began to rise as had been noted before, slowly at first and rapidly after about two hours, until it levelled off at about 925 mv. Thus, as the sample had had ample time to swell overnight, it must have been some effect on the indicator electrode which caused the sudden rise in E.M.F.

Residual Acidity at 550° and 600°C

In all the series it was found that 0.3 to 0.4 milliequivalents per gram of acidity still remained after carbonization to 600°C. At 550°C the quantity was usually slightly higher.

It was originally thought to be a remnant of the weaker component acidity. This was suggested by the lower half neutralization potential which has been used as an indication of acidic strength (cf. A. J. Martin, 1957). Later it was found that the half neutralization potential varied considerably, even in different titrations of the same sample.

Therefore the 500°C cokes from each of the fresh coals were titrated in admixture with benzoic acid. Only one inflection was obtained in each case, indicating that the residual acidic groups were of about the same strength as benzoic acid in ethylenediamine.

They would thus seem to be remnants of the original stronger rather than weaker component acidity, at least for samples M, N, and O.

Sample P may be an exception in this regard, as the original weaker component acidity could barely be differentiated from the stronger, which was present in very small amount. When the fresh coal was titrated with benzoic acid only one inflection was obtained, showing that both component acidities were strong enough to

titrate with it. The residual acidity could be derived from either, but as the stronger is present in small amount in the coal it may well come from the weaker.

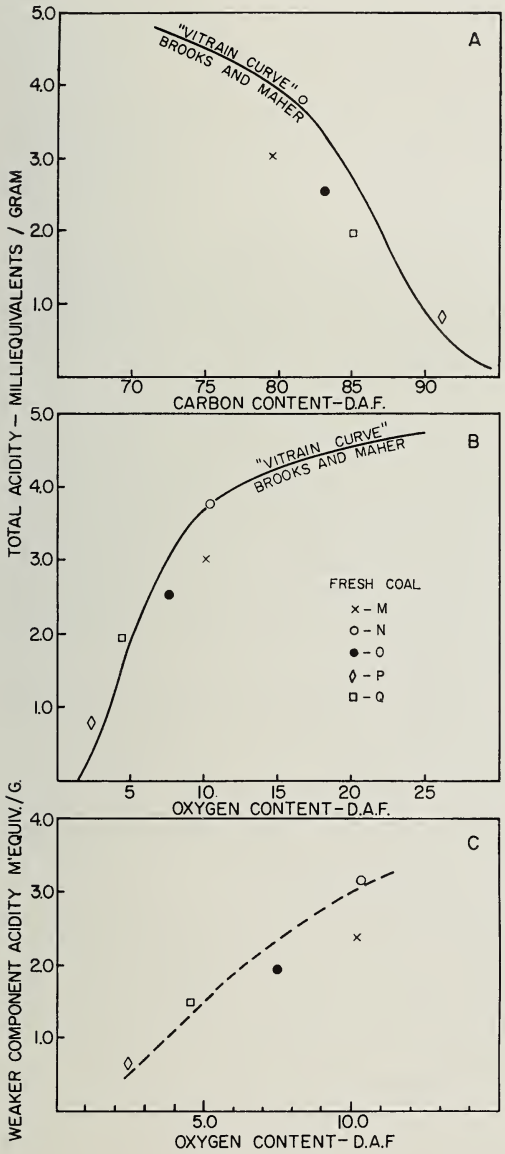


Fig. 31.—Variation of the acidities of the fresh coals with carbon and oxygen content.

A. Total acidity vs. carbon content.

B. Total acidity vs. oxygen content.

C. Weaker component acidity vs. oxygen content.

Of course the possibility also exists that the residual acidity could be due to new strongly acidic groups formed in the pyrolysis and having no connection with groups originally present in the coal.

CAUSTIC SOLUBILITIES OF THE FRESH AND OXIDIZED COALS

Each of the fresh and oxidized coals (5 grams) was brought to the boil in 10 percent sodium hydroxide solution (100 ml) and the suspension filtered through two layers of filter paper.

All samples gave colorless or light straw-colored solutions except forced oxidized coals M, N, and O, which gave very dark brown solutions typical of alkaline humates. Even in the cold these samples gave brown solutions.

The failure of forced oxidized coal Sample P to show this pronounced caustic solubility is noteworthy as it probably indicates that no significant formation of carboxyl groups took place during oxidation.

RELATION OF ACIDITY OF FRESH COALS TO RANK

In figures 31*a* and 31*b*, the total acidities of the fresh coals are plotted against carbon content and oxygen content. For comparison the "vitrain curves," according to J. D. Brooks and T. P. Maher (1957), are shown in the same figures.

Coals N and P fall just above the carbon curve whereas the other coals fall below it.

The coals fall closer to the oxygen curve, but Samples M and O are noticeably below it. These are the coals with the highest percentages of organic sulfur.

The stronger component acidity was of the same order (0.60 to 0.65 milliequivalents per gram) for the three lowest rank coals but decreased for coals with increase in rank.

Figure 31*c* shows the weaker component acidities graphed against oxygen content. Here also coals M and O fall below the curve.

SUMMARY AND CONCLUSIONS

Fresh Coals

All five coals behaved as dibasic acids in ethylenediamine. The differentiation between strongly acid and weakly acid groups was distinct for the high-volatile coals, less so for the low-volatile coal of low acidity.

The total acidity generally correlated with rank, decreasing as the rank increased. The weaker component acidity appeared to correlate with rank better than the stronger. Coals with a large content of organic sulfur had lower acidity than might be expected on the basis of their carbon or even oxygen content.

Carbonization of Fresh Coals

In the carbonization of the three high-volatile coals the acidity due to the original two component acidities began to decrease above 200°C. The greatest decrease was from 400° to 500°C, but, after 400° or 450°C, differentiation between them was no longer obtained. Groups of weaker strength made their appearance as early as 300°C in one coal and at 400°C for the other two. They persisted to 500°C for the two coals of lowest rank. The tendency of the weak groups to appear seemed to diminish as the rank increased, and they were not found in the carbonized products from the low-volatile coal. However, in the low-volatile series groups of the same strength as those of the original weaker acidity (which had vanished above 300°C) reappeared at 500°C with a resulting small increase in total acidity at that temperature.

Natural Oxidation

Oxidation at room temperature in general caused an initial decrease in acidity followed by a slow rise. The over-all result was a small decrease except for Sample O where there was a slight increase.

Chemical and physical properties were not greatly changed except for Gieseler plasticity, which was decreased. This was most marked for Sample M where the ability to form frothy cokes at 400° and 550°C was also lost.

Effect of Natural Oxidation on Carbonization

Oxidation at room temperature did not cause much change in the cokes obtained on carbonization, except for Sample M as stated above.

There seemed to be a tendency for natural oxidation to lessen the number of very weak groups formed in carbonization and to narrow the temperature range over which they were found.

The acidity remaining at 500°C was less for the oxidized coal series than for the fresh, except for Sample O where the two series were very similar.

Forced Oxidation

Oxidation at 110°C increased the oxygen content to more than double its original value in all samples, but Sample O (high-volatile A bituminous) showed the largest percentage increase. There were decreases in volatile matter and calorific value, and all measurable plastic and swelling properties were lost.

Sample O showed the largest percentage increase in total acidity. However, in all the oxidized coals the percentage of oxygen in acidic form was somewhat less than in the fresh coals, so more of the oxygen must have been taken up into non-acidic than acidic structures.

In Samples M and N practically all of the increase was in the stronger component acidity. For the three high-volatile coals the infrared spectra indicated the formation of carboxyl groups which would be responsible for at least part of this increase. In Sample M the stronger component acidity could eventually be differentiated into two separate acidities, the weaker of which appeared to be due to carboxyl groups.

In coals O and P the weaker acidity showed an appreciable increase although that of the stronger acidity was still greater.

Effect of Forced Oxidation on Carbonization

Carbonization of the forced oxidized coals gave only chars for all samples.

The increase in the stronger component acidity, which was most probably due largely to the formation of carboxyl groups in the three high-volatile coals, was thought to be related to loss of coking ability.

The acidity remaining at 500°C was less for the oxidized coal series than for the fresh, except for Sample O where it was about the same.

The number and amount of very weak acidic groups formed in the carbonization of the high-volatile coals and the temperature ranges over which they persisted were different in the fresh and oxidized coals. However, no simple pattern in the variations could be seen.

Nature of the Acidic Groups

The presence of groups of two distinct acidic strengths, particularly in the fresh high-volatile coals, was noteworthy. There was no evidence that the stronger groups were carboxyl. Perhaps they were phenolic groups with their strength enhanced because of their positions in the structure. The weaker groups would be those of more normal strength.

It was noted that no indication of hydroperoxides could be detected in the oxidized coals. According to the work of A. J. Martin (1957) such groups would be expected to titrate as very weak acids.

The presence of carboxyl groups was indicated in the high-volatile coals after forced oxidation.

The nature of the very weak groups, formed in the carbonization of the high-volatile coals, is not known. Perhaps they are very weak phenolic groups formed during decomposition.

The infrared spectra were not found to be very satisfactory for following the behavior of the hydroxyl groups. Even when water was excluded the absorption band was so broad that even semi-quantitative appraisal was difficult.

The possibility of the presence of some other functional groups capable of titration should not be overlooked, but their contribution, if any, is likely to be small. Acidity associated with nitrogen or hydrocarbon structures may possibly be partly responsible for the small amount found after carbonization to 600°C.

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APPENDIX

TABULAR DATA

TABLE 1.—SAMPLE M, FRESH COAL CARBONIZATION SERIES
Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength					Percent of coal		Acidic oxygen as % of total oxygen
							Total oxygen (by diff.)	Acidic oxygen (Assuming one oxygen atom per equivalent)	
Fresh	3.35	0.78	2.57						
Coal	3.37	0.85	2.52						
Mean	3.36	0.82	2.54				10.18	5.38	52.8
200	3.52	0.97	2.55						
	3.55	0.98	2.57						
Mean	3.54	0.98	2.56				10.75	5.66	52.7
300	3.30	0.82	2.48						
	3.21	0.77	2.44						
Mean	3.26	0.80	2.46				10.55	5.22	49.5
350	2.86	0.70	2.16						
	2.86	0.64	2.22						
Mean	2.86	0.67	2.19				9.49	4.58	48.3
400	3.03	0.63	1.61	0.79					
	3.00	0.73	1.58	0.69					
Mean	3.02	0.68	1.60	0.74			8.45	4.83	57.2
450	3 45	2.01		0.87		0.57			
	3.45	1.99			1.46				
Mean	3.45	2.00		0.87		0.58	7.11	5.52	77.6
500	3.06	0.78	1.68			0.60			
	3.00	0.82		2.18					
Mean	3 03	0.80	1.65			0.58	6.14	4.85	79 0
550	0 58	0.58							
	0 59	0 59							
Mean	0 59	0.59					5.69	0 94	16 5
600	0 32	0 32							
	0 37	0.37							
Mean	0 35	0.35					4.36	0 56	12.8

Table 2.—Sample M, Variation of Acidity During Natural Oxidation.
Values in milliequivalents per gram of dry, ash-free coal.

Time exposed (days)	Total acidity	Component acidities in order of decreasing acidic strength	
0	3.36	0.82	2.54
18	3.02	0.68	2.34
41	2.98	0.70	2.28
64	3.03	0.63	2.40

Table 3.—Sample M, Naturally Oxidized Coal Carbonization Series.
Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength			Percent of coal: Total oxygen (by diff.)	Percent of coal: Acidic oxygen (Assuming one oxygen atom per equivalent)	Acidic oxygen as % of total oxygen
Nat. Oxid. Coal	3.06	0.62	2.44				
	3.00	0.64	2.36				
Mean	3.03	0.63	2.40		11.38	4.85	42.6
200	3.24	0.81	2.43				
	3.17	0.77	2.40				
Mean	3.21	0.79	2.42		11.37	5.14	45.2
300	3.06	0.67	2.39				
	3.08	0.61	2.47				
Mean	3.07	0.64	2.43		11.22	4.91	43.8
350	2.72	0.58	2.14				
	2.96	0.59	2.37				
Mean	2.84	0.59	2.25		10.85	4.54	41.8
400	3.14	0.89	1.47	0.78			
	2.97	0.68	1.53	0.76			
Mean	3.06	0.79	1.50	0.77	10.35	4.90	47.3
450	2.03	1.49		0.54			
	1.99	1.56		0.43			
Mean	2.01	1.53		0.48	8.35	3.22	38.6
500	0.96	0.96					
	1.09	1.09					
Mean	1.03	1.03			7.21	1.65	22.9
550	0.54	0.54					
	0.55	0.55					
Mean	0.55	0.55			5.37	0.88	16.4
600	0.38	0.38					
	0.35	0.35					
Mean	0.37	0.37			3.51	0.59	16.8

TABLE 4.—SAMPLE M, VARIATION OF ACIDITY DURING FORCED OXIDATION.

Values in milliequivalents per gram of dry, ash-free coal.

Time exposed (days)	Total acidity	Component acidities in order of decreasing acidic strength		
0	3.36	0.82		2.54
9	3.50	1.49		2.01
34	4.12	1.78		2.34
47	4.15	0.69	1.37	2.09

TABLE 5.—SAMPLE M, FORCED OXIDIZED COAL CARBONIZATION SERIES.

Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength					Percent of coal		Acidic oxygen as % of total oxygen
							Total oxygen (by diff.)	Acidic oxygen	
								Based on assumption stated in text, p. 21	
Forced Oxid.	4.15	0.62	1.39	2.14					
Coal	4.15	0.76	1.34	2.05					
Mean	4.15	0.69	1.37	2.09			20.29	8.83	43.5
200	3.82	0.52	1.41	1.89					
	3.91	0.51	1.50	1.90					
Mean	3.87	0.52	1.45	1.90			19.78	8.51	43.0
300	4.21	0.60	1.01	1.37	1.23				
	4.15	0.60	1.13	1.31	1.11				
Mean	4.18	0.60	1.07	1.34	1.17		17.12	8.40	49.1
350	3.83	1.53		0.95	1.35				
	3.94	1.48		1.17	1.29				
Mean	3.89	1.51		1.06	1.32		15.22	7.72(?)	50.7(?)
400	5.29	1.56		1.62	2.11				
	5.24	1.61		1.63	2.00				
Mean	5.27	1.59		1.63	2.05		13.26	10.02(?)	75.6(?)
450	3.62		1.84		1.78				
	3.45		1.79		1.66				
Mean	3.54		1.82		1.72		10.33	5.66	54.8
500	0.65		0.65						
	0.71		0.71						
Mean	0.68		0.68				8.16	1.09	13.4
550	0.30		0.30						
	0.33		0.33						
Mean	0.32		0.32				6.02	0.51	8.5
600	0.36		0.36						
	0.36		0.36						
Mean	0.36		0.36				4.83	0.58	12.0

Table 6.—Sample N, Fresh Coal Carbonization Series.
Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength					Percent of coal		Acidic oxygen as % of total oxygen
							Total oxygen (by diff.)	Acidic oxygen (Assuming one oxygen atom per equivalent)	
Fresh	3.79	0.64	3.15						
Coal	3.77	0.66	3.11						
Mean	3.78	0.65	3.13				10.36	6.05	58.4
200	3.69	0.66	3.03						
	3.70	0.72	2.98						
Mean	3.70	0.69	3.01				10.92	5.92	54.2
300	5.61	0.78	2.84			1.99			
	5.58	0.81	2.84			1.93			
Mean	5.60	0.80	2.84			1.96	11.59	8.96	77.3
350	4.91	0.78	2.40			1.73			
	5.00	0.64	2.58			1.78			
Mean	4.96	0.71	2.49			1.76	10.90	7.94	72.8
400	4.39	0.58	2.01		0.71	1.09			
	4.45	0.67	1.96		0.58	1.24			
Mean	4.42	0.63	1.93		0.65	1.16	10.11	7.07	69.9
450	2.42	1.19	0.63		0.60				
	2.66	1.23	0.91		0.52				
	2.77	1.23	0.95		0.59				
Mean	2.62	1 22	0.83		0.57		8.51	4.19	49.2
500	2.36	0.94		1.42					
	1.92	0.95		0.97					
	2.59	0.85		1.74					
Mean	2.29	0.91		1.38			6.21	3.66	58.9
550	0.58	0.58							
	0.57	0.57							
	0.44	0.44							
Mean	0.53	0.53					4.74	0.85	17.9
600	0.35	0.35							
	0.55	0.55							
	0.41	0.41							
Mean	0.44	0.44					4.56	0.70	15.4

TABLE 7.—SAMPLE N, VARIATION OF ACIDITY DURING NATURAL OXIDATION.
Values in milliequivalents per gram of dry, ash-free coal.

Time exposed (days)	Total acidity	Component acidities in order of decreasing acidic strength	
0	3.78	0.65	3.13
26	3.22	0.56	2.66
44	3.51	0.87	2.64
64	3.68	0.82	2.86

TABLE 8.—SAMPLE N, NATURALLY OXIDIZED COAL CARBONIZATION SERIES.
Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength			Percent of coal		Acidic oxygen as % of total oxygen
					Total oxygen (by diff.)	Acidic oxygen (Assuming one oxygen atom per equivalent)	
Nat. Oxid. Coal	3.66	0 83	2.83				
	3 70	0 81	2.89				
Mean	3.68	0 82	2.86		10.88	5.89	54.1
200	3 62	0 83	2 79				
	3 62	0 82	2 80				
Mean	3 62	0 83	2.79		10.62	5.79	54.5
300	3 47	0 91	2 56				
	3.47	0 84	2 63				
Mean	3 47	0 88	2.59		10.56	5.55	52.6
350	3 61	0 82	2 05	0.74			
	3 65	0 82	2 29	0 54			
Mean	3 63	0 82	2.17	0 64	10.05	5.81	57.8
400	3 14	0 83	1 34	0.97			
	3 20	0 71	1 45	1 04			
Mean	3 17	0.77	1.40	1 00	8.62	5.07	58.8
450	2 38	1.19		1 19			
	2 42	1 23		1 19			
Mean	2 40	1 21		1.19	7.75	3.84	49.5
500	0 77	0 77					
	0 80	0 80					
Mean	0 79	0 79			5 99	1.26	21 0
550	0 29	0 29					
	0 30	0 30					
Mean	0 30	0 30			4.18	0.48	11.5
600	0 37	0 37					
	0 32	0 32					
Mean	0 35	0.35			3.69	0.56	15 2

Table 9.—Sample N, Variation of Acidity During Forced Oxidation.

Values in milliequivalents per gram of dry, ash-free coal.

Time exposed (days)	Total acidity	Component acidities in order of decreasing acidic strength	
0	3.78	0.65	3.13
17	4.43	1.58	2.85
35	5.05	1.62	3.43
47*	5.37	2.08	3.29

*Ten ml of benzene used to facilitate titration.

Table 10.—Sample N, Forced Oxidized Coal Carbonization Series.

Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength			Percent of coal		Acidic oxygen as % of total oxygen
					Total oxygen (by diff.)	Acidic oxygen	
						Based on assumption stated in text, p. 32	
Forced Oxid.	5.37	2.06	3.31				
Coal*	5.37	2.09	3.28				
Mean	5.37	2.08	3.29		20.43	10.61	51.9
200	5.01	2.34	2.67				
	5.16	2.13	3.03				
	5.19	1.99	3.20				
Mean	5.12	2.15	2.97		19.61	10.30	52.5
300	4.34	1.66	2.68				
	4.36	2.03	2.33				
Mean	4.35	1.85	2.50		16.85	8.51	50.5
350	3.78	1.31	1.91	0.56			
	3.80	1.46	1.88	0.46			
Mean	3.79	1.39	1.90	0.50	15.18	6.97	45.9
400	2.69	0.95	1.74				
	2.61	0.96	1.65				
Mean	2.65	0.96	1.69		12.42	4.54	36.6
450	1.43	0.96	0.47				
	1.43	0.98	0.45				
Mean	1.43	0.97	0.46		10.14	2.29	22.6
500	0.39	0.39					
	0.34	0.34					
Mean	0.37	0.37			7.81	0.59	7.6
550	0.38	0.38					
	0.27	0.27					
Mean	0.33	0.33			6.25	0.53	8.5
600	0.29	0.29					
	0.24	0.24					
Mean	0.27	0.27			4.19	0.43	10.3

*10 ml benzene used in titration to avoid stickiness.

TABLE 11.—SAMPLE O, FRESH COAL CARBONIZATION SERIES.
Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength						Percent of coal		Acidic oxygen as % of total oxygen
								Total oxygen (by diff.)	Acidic oxygen (Assuming one oxygen atom per equivalent)	
Fresh	2.61	0.60			2.01					
	2.52	0.60			1.92					
Coal	2.50	0.59			1.91					
Mean	2.54	0.60			1.94			7.52	4.06	54.0
200	2.62	0.60			2.02					
	2.62	0.64			1.98					
Mean	2.62	0.62			2.00			8.04	4.19	52.1
300	2.47	0.50			1.97					
	2 50	0 51			1.99					
Mean	2 49	0 51			1.98			8.02	3.98	49.6
350	2 25	0.55			1.70					
	2 30	0.68			1.62					
Mean	2 28	0.62			1.66			7.91	3.65	46.1
400	2 32	0.86	0 49			0.97				
	2.53	0.88	0 69			0.96				
	2.35	0 60	0.50		0.46		0.79			
	2.60	0 76		1.08			0.77			
Mean	2 45	0.78			1.67			6.97	3.92	56.2
450	1.39	0.70			0.69					
	1.68	0 68			1.00					
	1.51	0 82			0.69					
Mean	1.53	0.73			0.80			5.96	2.45	41.1
500	0 36		0.36							
	0 37		0 37							
Mean	0.37		0 37					5.13	0.59	11.5
550	0.33		0 33							
	0 31		0.31							
Mean	0.32		0.32					3.52	0.51	14.5
600	0.59		0 59							
	0.31		0 31							
Mean	0.45		0.45					2.85	0.72	25.3

TABLE 12.—SAMPLE O, VARIATION OF ACIDITY DURING NATURAL OXIDATION.
Values in milliequivalents per gram of dry, ash-free coal.

Time exposed (days)	Total acidity	Component acidities in order of decreasing acidic strength		
0	2.54	0 60	1 94	
12	2 08	0 46	1 62	
21	1 82	0 55	1 27	
30	2 03	0 66	1 37	
37	1 83	0 57	1 26	
48	2 09	0 41	0 99	0.69
64	2 62	0 68	1 94	

TABLE 13.—SAMPLE O, NATURALLY OXIDIZED COAL CARBONIZATION SERIES.
Acidities in milliequivalents per gram.
All values based on dry, ash free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength					Percent of coal		Acidic oxygen as % of total oxygen
							Total oxygen (by diff.)	Acidic oxygen (Assuming one oxygen atom per equivalent)	
Nat. Oxid. Coal	2.67	0.67		2 00					
	2 56	0.68		1 88					
Mean	2 62	0.68		1 94			7 61	4.19	55 1
200	2 71	0 80		1 91					
	2 70	0.71		1 99					
Mean	2.71	0.76		1 95			8.13	4.34	53.4
300	2 68	0 79		1 89					
	2 58	0 65		1 93					
Mean	2 63	0.72		1 91			8 40	4.21	50.1
350	2 22	0 75		1 47					
	2 24	0 66		1 58					
	2 37	0 52		1 85					
	2 38	0.60		1 78					
Mean	2 30	0 63		1 67			7 91	3.68	46.5
400	2 53	0 60		0 99		0 94			
	2 56	0 53		1 11	0 28	0 64			
	2 82	0 54		1 30		0 98			
	2 75	0 61		1 30		0 84			
Mean	2.67	0 57		1.18		0 92	7 40	4 27	57.7
450	1 64		0 84			0 80			
	1 64		0 92			0 72			
Mean	1 64		0 88			0.76	5 73	2.62	45 7
500	0 57		0 57						
	0 58		0 58						
Mean	0.58		0 58				4 87	0 93	19 1
550	0 40		0 40						
	0 37		0 37						
Mean	0 39		0 39				3 93	0 62	15 8
600	0 44		0 44						
	0 48		0 48						
Mean	0 46		0 46				3 37	0 74	22 0

Table 14.—Sample O, Variation of Acidity During Forced Oxidation.

Values in milliequivalents per gram of dry, ash-free coal.

Time exposed (days)	Total acidity	Component acidities in order of decreasing acidic strength	
0	2 54	0 60	1 94
14	3 89	1 38	2 51
27	4 32	1 80	2 52
36	4 39	1 85	2 54
47	4 47	2 02	2 45

Table 15.—Sample O, Forced Oxidized Coal Carbonization Series.

Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength					Percent of coal		Acidic oxygen as % of total oxygen
							Total oxygen (by diff.)	Acidic oxygen	
								Based on assumption stated in text, p. 41	
Forced	4 39	2 01		2.38					
Oxid.	4 55	2 07	0.72		1.76				
Coal	4 38	1 79	0.95		1.64				
	4 54	2 20	1.34		1.00				
Mean	4 47	2 02		2.45			18.28	9 30	50.9
200	4 11	2 01		2.10					
	4 19	2 10	1 06		1.03				
	4 29	2 16	0 97		1.16				
Mean	4 20	2 09		2.11			20.99	8.85	42 2
300	4 00	1 34		1 93		0 73			
	4 03	1 27		2 02		0 74			
Mean	4 02	1 30		1 98		0 74	14.85	7.36	49.6
350	5 11	1.28		1 65		2 18			
	5 06	1 22		1 59		2 25			
Mean	5 09	1 25		1.62		2 22	13.08	9.14	69.9
400	2.47	1 00		1 06		0 41			
	2 66	0 97		1 17		0 52			
	2.63	0 97		1.19		0 52			
Mean	2 59	0 98		1.14		0 48	10.67	4.82	45.2
450	2 03	0 84			1.19				
	2 03	0 84			1.19				
Mean	2 03	0 84			1.19		9 05	3.25	35 9
500	0 35		0 35						
	0 40		0 40						
Mean	0 38		0 38				6.54	0.61	9.3
550	0 27		0.27						
	0 28		0 28						
Mean	0 28		0 28				4.80	0 45	9.4
600	0 28		0 28						
	0 27		0 27						
Mean	0 28		0 28				3.45	0.45	13 0

Table 16.—Sample P, Fresh Coal Carbonization Series.
Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength			Percent of coal		Acidic oxygen as % of total oxygen
					Total oxygen (by diff.)	Acidic oxygen (Assuming one oxygen atom per equivalent)	
Fresh	0.85	0.14		0.71			
Coal	0.81	0.15		0.66			
Mean	0.83	0.15		0.68	2.45	1.33	54.3
200	0.81	0.30		0.51	2.41	1.30	53.9
300	0.79	0.26		0.53	2.50	1.26	50.4
350	0.40		0.40				
	0.44		0.44				
Mean	0.42		0.42		2.26	0.67	29.6
400	0.48		0.48				
	0.33		0.33				
	0.41		0.41				
Mean	0.41		0.41		2.50	0.66	26.4
450	0.41		0.41				
	0.63		0.63				
Mean	0.55		0.55		2.45	0.88	35.9
500	0.78	0.25		0.53			
	0.69	0.25		0.44			
Mean	0.74	0.25		0.49	2.70	1.18	43.7
550	0.35		0.35		2.27	0.56	24.7
600	0.32		0.32		2.61	0.51	19.5

Table 17.—Sample P, Naturally Oxidized Coal Carbonization Series.
Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength				Percent of coal		Acidic oxygen as % of total oxygen
						Total oxygen (by diff.)	Acidic oxygen (Assuming one oxygen atom per equivalent)	
Nat. Oxid. Coal	0.64	0 02		0.62				
	0.60	0.16		0.44				
Mean	0.62	0.09		0.53		2.10	0.99	47.1
200	0 69	0 04		0.65				
	0 87	0 04	0.43		0.40			
Mean	0 78	0 04		0.74		2.09	1.25	59.8
300	0.46	0 01		0.45				
	0.46	0 01		0.45				
Mean	0.46	0 01		0.45		2.27	0.74	32.6
350	0 40		0 40					
	0 40		0 40					
Mean	0 40		0 40			2.05	0.64	31.2
400	0 42		0 42					
	0 44		0 44					
Mean	0.43		0 43			2.26	0.69	30.5
450	0 48		0 48					
	0 45		0 45					
Mean	0.47		0 47			2.19	0.75	34.2
500	0 43		0 43					
	0 52		0 52					
Mean	0 48		0 48			2 33	0.77	33.0
550	0 30		0 30					
	0 25		0 25					
Mean	0 28		0 28			2.81	0.45	16.0
600	0 32		0 32			2 61	0 51	19.5

Table 18.—Sample P, Variation of Acidity During Forced Oxidation.
Values in milliequivalents per gram of dry, ash-free coal.

Time exposed (days)	Total acidity	Component acidities in order of decreasing acidic strength		
0	0 83	0.15	0.68	
37	1 19	0 34	0 85	
47	1 58	0 55	0.52	0.51

Table 19.—Sample P, Forced Oxidized Coal Carbonization Series.
Acidities in milliequivalents per gram.
All values based on dry, ash-free coal.

Carb. temp. °C	Total acidity	Component acidities in order of decreasing acidic strength	Percent of coal: Total oxygen (by diff.)	Percent of coal: Acidic oxygen (Based on assumption stated in text, p. 51)	Acidic oxygen as % of total oxygen
Forced	1.59	0.54 1.05			
Oxid.	1.49	0.55 0.53 0.41			
Coal	1.66	0.56 0.51 0.59			
Mean	1.58	0.55 0.52 0.51	5.92	2.53	42.7
200	1.43	0.54 0.89			
	1.30	0.51 0.79			
	1.56	0.57 0 99			
Mean	1.43	0.54 0 89	5.70	2.29	40.2
300	1 32	0 49 0 83			
	1 13	0 46 0.67			
	1 24	0 46 0 78			
Mean	1 23	0 47 0.76	4.77	1.97	41.3
350	1 06	0.32 0.74			
	1 07	0.45 0.62			
	1 12	0 37 0.75			
Mean	1 08	0 38 0 70	4.32	1.73	40.0
400	0 80	0.40 0.40			
	0 80	0 34 0.46			
	0 84	0 33 0.51			
	0 85	0.32 0.53			
Mean	0 82	0.35 0.47	4.02	1.31	32.6
450	0.65	0.65			
	0 65	0.65			
	0 75	0.75			
Mean	0.68	0.68	3 05	1.09	35.7
500	0.49	0.49			
	0.48	0.48			
	0 43	0.43			
Mean	0.47	0.47	2.13	0.75	35.2
550	0.34	0.34			
	0.40	0.40			
Mean	0.37	0.37	2.08	0.59	28.4
600	0 32	0.32			
	0 29	0.29			
Mean	0.31	0.31	2 97	0 50	16.8

Table 20.—Fresh Sample M, Analytical Data for Coal and Carbonized Products.

	Percent
Moisture (as received)	14.3
Vol. matter (d.a.f.)	49.4
Forms of sulfur (d.a.f.):	
Sulfate	0.56
Pyritic	0.48
Organic	2.17
Total	3.21
Petrographic analysis:	
Vitrinite	95.5
Exinite	2.6
Inertinite	1.1
Mineral matter	0.8

Calorific value (d.a.f.):	
Btu/lb	14382
cal/g	7989
Gieseler plasticity:	
Softening temp.	353°C
Fusion temp.	391°C
Max. fluidity temp.	415°C
Setting temp.	469°C
Maximum Fluidity, dial div./min.	2320*
Free swelling index	3½

Carb. temp., °C	Ash (dry)	Dry, ash-free basis						Carbonization product
		C	H	N	S	O**	Wt. †	
Fresh coal	2.46	79.60	5.53	1.44	3.25	10.18	16.72	
200	2.80	78.99	5.51	1.43	3.32	10.75	16.55	Unconsolidated char
300	2.55	79.23	5.48	1.45	3.29	10.55	16.46	Unconsolidated char
350	2.60	80.57	5.40	1.46	3.08	9.49	15.78	Slightly consolidated char; broke up on handling
400	2.93	82.58	4.66	1.59	2.72	8.45	13.82	Very highly swollen coke; frothy texture, soft
450	3.31	84.67	3.97	1.68	2.57	7.11	12.11	Highly swollen coke; frothy texture, soft
500	3.54	86.51	3.40	1.70	2.25	6.14	11.48	Slightly swollen coke; moderately hard
550	4.95	87.36	3.05	1.71	2.19	5.69	11.30	Unswollen hard coke
600	4.69	89.08	2.65	1.70	2.21	4.36	10.99	Slightly shrunken hard coke

*Packed with 3 drops of benzene; swelled out of sample cup.
**Oxygen percentage obtained by difference.
†Grams obtained from 20 grams of coal charged to the retort.

TABLE 21.—NATURALLY OXIDIZED SAMPLE M, ANALYTICAL DATA FOR COAL AND CARBONIZED PRODUCTS.

	Percent
Moisture (as received)	2.7
Vol. matter (d.a.f.)	45.1
Calorific value (d.a.f.):	
Btu/lb	14299
cal/g	7944
Free swelling index	4

Gieseler plasticity:

Softening temp.	353°C
Fusion temp.	417°C
Max. fluidity temp.	427°C
Setting temp.	454°C

Maximum fluidity, dial div./min. . . 9*

Carb. temp., °C	Ash (dry)	Dry, ash-free basis						Carbonization product
		C	H	N	S	O**	Wt. †	
Coal	2.42	78.51	5.37	1.43	3.31	11.38	18.99	
200	2.69	78.45	5.32	1.46	3.40	11.37	18.74	Unconsolidated char
300	2.60	78.74	5.27	1.47	3.30	11.22	18.56	Unconsolidated char
350	2.70	79.46	5.09	1.48	3.12	10.85	17.89	Soft consolidated char
400	3.05	81.02	4.20	1.66	2.77	10.35	15.43	Soft unswollen coke
450	3 40	83.53	3.75	1.62	2.75	8.35	14.05	Moderately hard unswollen coke
500	3.52	85.38	3.31	1.64	2.46	7.21	13.29	Moderately hard slightly shrunken coke
550	4.03	87.53	2.99	1.75	2.36	5.37	12.79	Hard slightly shrunken coke
600	4.43	89.71	2.69	1.75	2.34	3.51	12.38	Hard slightly shrunken coke

*Packed with 6 drops of benzene.
**Oxygen percentage obtained by difference.
†Grams obtained from 20 grams of coal charged to the retort.

TABLE 22.—FORCED OXIDIZED SAMPLE M, ANALYTICAL DATA FOR COAL AND CARBONIZED PRODUCTS

	Percent
Moisture (as received)	2.1
Vol. matter (d.a.f.)	39.1
Free swelling index	0

Calorific value (d.a.f.):

Btu/lb	11931
cal/g	6628

Gieseler plasticity:
Unobtainable; coal non-agglomerating

Carb. temp., °C	Ash (dry)	Dry, ash-free basis						Carbonization product
		C	H	N	S	O**	Wt. †	
Coal	2.2	71.24	4.10	1.30	3.07	20.29	19.14	
200	2.3	71.73	4.08	1.35	3.06	19.78	18.78	Unconsolidated char
300	2.4	74.39	4.11	1.41	2.97	17.12	17.61	Unconsolidated char
350	2.7	76.44	4.02	1.44	2.88	15.22	16.70	Very slightly coherent char, crumbled on handling
400	2.7	78.79	3.78	1.55	2.62	13.26	15.67	Very slightly coherent char, crumbled on handling
450	2.8	81.98	3.53	1.64	2.52	10.33	14.72	Very slightly coherent char, crumbled on handling
500	3.3	84.46	3.29	1.70	2.39	8.16	13.92	Very slightly coherent char, crumbled on handling
550	3.8	86.95	2.91	1.71	2.41	6.02	13.22	Slightly coherent char, easily crushed
600	4.5	88.40	2.66	1.69	2.42	4.83	12.71	Slightly coherent char, easily crushed

**Oxygen percentage obtained by difference.
†Grams obtained from 20 grams of coal charged to the retort.

Table 23.—Fresh Sample N, Analytical Data for Coal and Carbonized Products.

	Percent
Moisture (as received)	8.0
Vol. matter (d.a.f.)	38.4
Forms of sulfur (d.a.f.):	
Sulfate	0.02
Pyritic	0.36
Organic	0.53
Total	0.91
Petrographic analysis:	
Vitrinite	91.6
Exinite	4.6
Inertinite	2.8
Mineral matter	1.0

Calorific value (d.a.f.):	
Btu/lb	14452
cal/g	8029
Gieseler plasticity:	
Softening temp.	383°C
Fusion temp.	407°C
Max. fluidity temp.	424°C
Setting temp.	456°C
Maximum fluidity, dial div./min.	27
Free swelling index	4

Carb. temp., °C	Ash (dry)	Dry, ash-free basis C	H	N	S	O**	Wt.†	Carbonization product
Coal	9.7	81.59	5.19	1.90	0 96	10 36	20.77	
200	9 9	81.10	5.22	1.84	0 92	10.92	20.66	Unconsolidated char
300	10 0	80.55	5.10	1.81	0 95	11.59	20.41	Unconsolidated char
350	10 1	81.35	5.02	1.82	0 91	10.90	19.99	Slightly consolidated char, broke up on handling
400	11 1	82 71	4.40	1.96	0.82	10 11	17.90	Soft unswollen coke
450	12 1	84.72	3 89	2.07	0.81	8 51	16.28	Moderately hard slightly shrunken coke
500	13 0	87 47	3 46	2.15	0.71	6.21	15.35	Hard slightly shrunken coke
550	15 0	89 42	3.02	2.12	0.70	4.74	14.53	Hard slightly shrunken coke
600	15.6	89.80	2.84	2.05	0.75	4.56	14.15	Hard slightly shrunken coke

**Oxygen percentage obtained by difference.
†Grams obtained from 25 grams of coal charged to the retort.

Table 24.—Naturally Oxidized Sample N, Analytical Data for Coal and Carbonized Products.

	Percent
Moisture (as received)	2.6
Vol. matter (d.a.f.)	37.5
Calorific value (d.a.f.):	
Btu/lb	14367
cal/g	7982
Free swelling index	4

Gieseler plasticity:	
Softening temp.	397°C
Fusion temp.	—
Max. fluidity temp.	413°C
Setting temp.	453°C
Maximum fluidity, dial div./min.	2

Carb. temp., °C	Ash (dry)	Dry, ash-free basis C	H	N	S	O**	Wt.†	Carbonization product
Coal	9 8	80 96	5.25	1.84	1.07	10.88	21.97	
200	9.9	81 23	5.26	1.89	1 00	10.62	21.84	Unconsolidated char
300	10.0	81 35	5.27	1.79	1 03	10.56	21 72	Unconsolidated char
350	10 0	82 08	5.19	1.74	0.94	10 05	21.16	Very slightly consolidated char, broke up on handling
400	11.0	84.13	4.54	1.88	0.83	8.62	18.89	Soft unswollen coke
450	12.0	85 45	3.93	2.03	0.84	7 75	17.37	Moderately hard unswollen coke
500	12.8	88.33	3.56	2.06	0.71	5 34	16 42	Moderately hard slightly shrunken coke
550	13.9	90.57	3.11	2.11	0.67	3 54	15 63	Moderately hard slightly shrunken coke
600	14.8	90.97	2.73	2.12	0.70	3 48	15 15	Moderately hard slightly shrunken coke

**Oxygen percentage obtained by difference.
†Grams obtained from 25 grams of coal charged to the retort.

Table 25.—Forced Oxidized Sample N, Analytical Data for Coal and Carbonized Products.

	Percent
Moisture (as received)	2.7
Vol. matter (d.a.f.)	36.3
Free swelling index	0

Calorific value (d.a.f.):
Btu/lb 11924
cal/g 6624

Gieseler plasticity:
Unobtainable; coal nonagglomerating

Carb. temp., °C	Ash (dry)	Dry, ash-free basis C	H	N	S	O**	Wt.†	Carbonization product
Coal	9 1	73 03	3 89	1.74	0 91	20 43	22 09	
200	9.3	73 80	3.89	1.72	0 98	19 61	21 66	Unconsolidated char
300	9 8	76.43	3.92	1.86	0.94	16.85	20 27	Unconsolidated char
350	10.1	78 19	3.80	1.90	0 93	15 18	19 34	Unconsolidated char
400	10.7	80.94	3.69	2 00	0 95	12 42	18 42	Unconsolidated char
450	11.2	83 28	3.50	2.12	0.96	10 14	17 35	Unconsolidated char
500	11.7	85.99	3.19	2 15	0 86	7 81	16 69	Unconsolidated char
550	13.1	87 65	3 09	2 20	0 81	6 25	15.71	Unconsolidated char
600	11.6	90 21	2 65	2.17	0 78	4 19	15.61	Unconsolidated char

**Oxygen percentage obtained by difference.
†Grams obtained from 25 grams of coal charged to the retort.

Table 26.—Fresh Sample O, Analytical Data for Coal and Carbonized Products.

	Percent
Moisture (as received)	2.4
Vol. matter (d.a.f.)	42.5
Forms of sulfur (d.a.f.):	
Sulfate	0.00
Pyritic	0 33
Organic	1.84
Total	2.17
Petrographic analysis:	
Vitrinite	80.5
Exinite	5.4
Inertinite	10.2
Mineral matter	3.9

Calorific value (d.a.f.):
Btu/lb 15053
cal/g 8363

Gieseler plasticity:
Softening temp. . . . . 366°C
Fusion temp. . . . . 390°C
Max. fluidity temp. . . . . 445°C
Setting temp. . . . . 476°C

Maximum fluidity, dial div./min. . . —*

Free swelling index 7

Carb. temp., °C	Ash (dry)	Dry, ash-free basis C	H	N	S	O**	Wt.†	Carbonization product
Coal	4 7	83.17	5.55	1 58	2 18	7 52	23 28	
200	4.6	82.74	5.53	1.55	2 14	8 04	23.27	Unconsolidated char
300	4 7	82 79	5.47	1 57	2.15	8 02	22.81	Unconsolidated char
350	4.8	82.97	5 35	1 67	2 10	7.91	22 47	Slightly consolidated char
400	5.4	85 10	4.54	1 68	1 71	6 97	18.88	Highly swollen frothy coke
450	6.5	86 60	3.79	2 03	1 62	5 96	16 60	Very highly swollen frothy coke
500	7.6	87.89	3 31	2 12	1.55	5.13	15.66	Very highly swollen frothy coke
550	9 5	89.81	3 05	2 01	1.61	3.52	15.52	Very highly swollen frothy coke
600	11 6	90.94	2.56	2 05	1.60	2.85	14.94	Very highly swollen frothy coke

*Most of coal swelled out of cup and into barrel.
**Oxygen percentage obtained by difference.
†Grams obtained from 25 grams of coal charged to the retort.

Table 27.—Naturally Oxidized Sample O, Analytical Data for Coal and Carbonized Products.

	Percent
Moisture (as received)	1.2
Vol. matter (d.a.f.)	42.5
Calorific value (d.a.f.):	
Btu/lb	14761
cal/g	8200
Free swelling index	8

Gieseler plasticity:

Softening temp.	375°C
Fusion temp.	398°C
Max. fluidity temp.	440°C
Setting temp.	478°C

Maximum fluidity, dial div./min. —*

Carb. temp., °C	Ash (dry)	Dry, ash-free basis C	H	N	S	O**	Wt.†	Carbonization product
Coal	4.6	83.01	5.56	1.67	2.15	7.61	23.60	
200	4.6	82.53	5.49	1.69	2.16	8.13	23.19	Unconsolidated char
300	4.7	82.36	5.39	1.70	2.15	8.40	23.13	Unconsolidated char
350	4.7	82.95	5.31	1.70	2.13	7.91	22.76	Slightly consolidated char
400	5.3	84.28	4.67	1.88	1.77	7.40	19.98	Highly swollen frothy coke
450	6.1	86.66	3.93	2.00	1.68	5.73	16.95	Very highly swollen frothy coke
500	7.1	88.10	3.42	2.06	1.55	4.87	15.70	Very highly swollen frothy coke
550	9.8	89.42	2.98	2.05	1.62	3.93	15.28	Very highly swollen frothy coke
600	11.3	90.46	2.60	2.01	1.56	3.37	14.95	Very highly swollen frothy coke

*Most of coal swelled out of cup and into barrel.
**Oxygen percentage obtained by difference.
†Grams obtained from 25 grams of coal charged to the retort.

Table 28.—Forced Oxidized Sample O, Analytical Data for Coal and Carbonized Products.

	Percent
Moisture (as received)	0.5
Vol. matter (d.a.f.)	35.7
Calorific value (d.a.f.):	
Btu/lb	12312
cal/g	6841
Free swelling index	0

Gieseler plasticity:
Unobtainable; coal nonagglomerating

Carb. temp., °C	Ash (dry)	Dry, ash-free basis C	H	N	S	O**	Wt.†	Carbonization product
Coal	4.4	74.20	4.09	1.45	1.98	18.28	23.85	
200	4.4	71.33	4.03	1.64	2.01	20.99	23.31	Unconsolidated char
300	4.7	77.40	4.14	1.66	1.95	14.85	21.97	Unconsolidated char
350	4.8	79.14	4.24	1.63	1.91	13.08	21.10	Unconsolidated char
400	5.2	81.78	4.03	1.68	1.84	10.67	19.64	Unconsolidated char
450	5.5	84.01	3.50	1.66	1.78	9.05	18.78	Unconsolidated char
500	6.4	86.87	3.18	1.69	1.72	6.54	17.66	Unconsolidated char
550	7.1	88.85	2.90	1.71	1.74	4.80	17.02	Unconsolidated char
600	7.8	90.58	2.51	1.72	1.74	3.45	16.32	Unconsolidated char

**Oxygen percentage obtained by difference.
†Grams obtained from 25 grams of coal charged to the retort.

TABLE 29.—FRESH SAMPLE P, ANALYTICAL DATA FOR COAL AND CARBONIZED PRODUCTS.

	Percent
Moisture (as received)	0.5
Vol. matter (d.a.f.)	18.9
Forms of sulfur (d.a.f.):	
Sulfate	0.00
Pyritic	0.03
Organic	0.53
Total	0.56
Petrographic analysis:	
Vitrinite	85.6
Exinite	0.0
Inertinite	13.4
Mineral matter	1.0

Calorific value (d.a.f.):	
Btu/lb	15647
cal/g	8693
Gieseler plasticity:	
Softening temp.	435°C
Fusion temp.	459°C
Max. fluidity temp.	475°C
Setting temp.	484°C
Maximum fluidity, dial div./min.	85*
Free swelling index	9

Carb. temp., °C	Ash (dry)	Dry, ash-free basis C	H	N	S	O**	Wt.†	Carbonization product
Coal	2 4	91.23	4 48	1.28	0.56	2 45	24.28	
200	2 6	91 36	4.48	1 16	0.59	2 41	24.08	Unconsolidated char
300	2 6	91.25	4.43	1.26	0.56	2.50	24.11	Unconsolidated char
350	2 6	91.50	4.46	1.21	0.57	2.26	24.10	Very slightly coherent char, easily crushed
400	2 6	91.44	4 40	1 08	0.58	2.50	23.93	Slightly coherent char broke up on handling
450	2 7	91 52	4 10	1.33	0.60	2.45	22.09	Moderately hard highly swollen coke
500	3 1	91 94	3 46	1.26	0.64	2.70	21.50	Moderately hard highly swollen coke
550	3 2	92 61	3.14	1.38	0.60	2.27	21.44	Moderately hard highly swollen coke
600	3 6	92 68	2.78	1.33	0.60	2.61	21.03	Moderately hard highly swollen coke

*Some of coal swelled into barrel.
**Oxygen percentage obtained by difference.
†Grams obtained from 25 grams of coal charged to the retort.

TABLE 30.—NATURALLY OXIDIZED SAMPLE P, ANALYTICAL DATA FOR COAL AND CARBONIZED PRODUCTS.

	Percent
Moisture (as received)	0.5
Vol. matter (d.a.f.)	19.5
Calorific value (d.a.f.):	
Btu/lb	15619
cal/g	8678
Free swelling index	9

Gieseler plasticity:	
Softening temp.	435°C
Fusion temp.	455°C
Max. fluidity temp.	477°C
Setting temp.	504°C
Maximum fluidity, dial div./min.	22

Carb. temp., °C	Ash (dry)	Dry, ash-free basis C	H	N	S	O**	Wt.†	Carbonization product
Coal	2.5	91.41	4.58	1.33	0.58	2.10	24.28	
200	2.5	91.39	4.56	1.39	0.57	2.09	24.05	Unconsolidated char
300	2.6	91.38	4.53	1.24	0.58	2.27	23 94	Unconsolidated char
350	2.8	91.57	4.52	1.27	0.59	2.05	23.79	Unconsolidated char
400	2.8	91 55	4.50	1.12	0.57	2 26	23.74	Slightly consolidated char broke up on handling
450	2.9	91 94	4.24	1.06	0.57	2 19	23.06	Moderately hard swollen coke
500	3.2	92.40	3.59	1.10	0.58	2.33	21.76	Moderately hard highly swollen coke
550	2.8	92.28	3.25	1.09	0 57	2.81	21.36	Moderately hard highly swollen coke
600	3 2	92 74	2.98	1.08	0 59	2.61	21 18	Moderately hard highly swollen coke

**Oxygen percentage obtained by difference.
†Grams obtained from 25 grams of coal charged to the retort.

Table 31.—Forced Oxidized Sample P, Analytical Data for Coal and Carbonized Products.

	Percent		
Moisture (as received)	0.7	Free swelling index	0
Vol. matter (d.a.f.)	19.0		
Calorific value (d.a.f.):		Gieseler plasticity:	
Btu/lb	14933	Unobtainable, coal nonagglomerating	
cal/g	8296		

Carb. temp., °C	Ash (dry)	Dry, ash-free basis						Carbonization product
		C	H	N	S	O**	Wt.†	
Coal	2.6	88 00	4.23	1.23	0.62	5.92	24 23	
200	2.5	88.19	4.21	1.31	0.59	5.70	24.08	Unconsolidated char
300	2.7	89.52	4.11	1.04	0.56	4.77	23.65	Unconsolidated char
350	2.8	90.00	4.12	1.01	0.55	4 32	23.43	Unconsolidated char
400	2.6	90.15	4 03	1.20	0.60	4.02	23.10	Unconsolidated char
450	2.9	91.26	3.87	1.23	0.59	3 05	22.47	Unconsolidated char
500	2.9	92.43	3.56	1.29	0.59	2.13	21 89	Unconsolidated char
550	3 2	92.71	3 24	1.37	0.60	2 08	21 21	Unconsolidated char
600	4.5	92.46	2.89	1.14	0.54	2.97	20.49	Unconsolidated char

**Oxygen percentage obtained by difference.
†Grams obtained from 25 grams of coal charged to the retort.

Table 32.—Fresh Sample Q, Analytical Data.

	Percent		
Moisture (as received)	4 6	Gieseler plasticity:	
Ash (dry)	11 5	Softening temp.	393°C
Vol. matter (d.a.f.)	37.3	Fusion temp.	414°C
		Max. fluidity temp.	443°C
Forms of sulfur (d.a.f.):		Setting temp.	477°C
Sulfate	0.15		
Pyritic	2 52		
Organic	0 63	Maximum fluidity, dial div./min.	2000
Total	3 30		
Calorific value:			
Btu/lb	15201	Free swelling index	6½
cal/g	8445		

Dry, ash-free basis				
C	H	N	S	O**
85.10	5.36	1.51	3.44	4.59

**Oxygen percentage obtained by difference.

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